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# Sludge Demetalization by the Union Carbide Corporation Electrochemical Process

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# SLUDGE DEMETALIZATION BY THE UNION CARBIDE CORPORATION ELECTROCHEMICAL PROCESS

by

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Contract No. 68-03-2968

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16. ABSTRACT

Laboratory-scale apparatus was designed and constructed to evaluate an electrochemical sludge demetalization process developed by Union Carbide to determine the desirable electrode and cell configurations which would remove the metals such as cadmium, nickel and zinc from municipal wastewater sludge. The quantity and quality of data obtained showed that the process was feasible but that additional work was necessary to make the process a production process.

Economics which were established based on the small amount of data obtained, indicated that the cadmium could be substantially removed at a piece of about 100 dollars per dry ton of sludge, which is not considered economically attractive at this time.

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## FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The purpose of this study was to investigate an electro-chemical process for the removal of heavy metals directly from sewage sludge without prior dewatering. Sludge does contain macronutrients useful to plant growth (such as nitrogen, phosphorus, and potassium). But it may also contain substantial quantities of metals, some of which (most notably cadmium, zinc, nickel, copper, and chromium) have been found to be toxic to vegetation at elevated concentrations and may accumulate in the human food chain. Concern over the migration of these elements into the food chain has resulted in the proliferation of many guidelines recommending limits on the amount of sludge applied to farmland based on the amount and species of metal contaminants involved. The objective of the Union Carbide demetalization process is to reduce the concentrations of such metals sufficiently to allow an increase in the amount of sludge that may be applied to the available acreage.

Francis T. Mayo, Director
Water Engineering Research Laboratory

## ABSTRACT

This research program was undertaken to evaluate and optimize the electrochemical sludge demetalization process developed by Union Carbide Corporation for the removal of toxic metals such as cadmium, nickel and zinc from municipal wastewater sludges.

A laboratory scale apparatus was designed and constructed to determine the most desirable electrode and cell operating conditions for the process tests and to investigate the various phenomena that occur during electrolysis. These tests were conducted using several reference electrode systems in a solution of distilled water and ions so that the process could be observed without the complications attendant to sludge. Dropping mercury and solid electrodes were used to generate linear polarization plots of current versus applied voltage to establish the plating potential appropriate for removing metal ions. This potential was determined to be -1.45 volts versus the $Cu\text{-}CuSO_4$ reference electrode.

An existing bench scale apparatus was modified to hold ~17 liters of fluid, and batch tests were conducted using both sludge and metal ion solution as the electrolyte. Efforts centered on achieving a metals balance during the experiments and on improving metal removal rates and coulombic efficiencies. Results were disappointing; however, since coulombic efficiencies remained below 10% and the metal removal performance was erratic. The use of the $Cu\text{-}CuSO_4$ reference electrode system to control total cell voltage (and thus, indirectly, the current density) did show promise. The quality and quantity of data obtained did not allow a strong correlation to be made between system design, operating parameters and process performance.

This report was submitted in fulfillment of Contract No. 68-03-2968 by Union Carbide Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1, 1980, to April 30, 1981, and work was completed as of December 31, 1982.

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Finally, Mr. Howard Wall, Project Officer, Environmental Research Center, U.S. Environmental Protection Agency, provided valuable guidance during the course of the contract.

# SECTION 1

# INTRODUCTION

The use of sewage sludge as a soil amendment has been practiced for many years in certain parts of the world. In the United States, recent studies reveal that up to 25% of the Nation's sludge production is disposed of on land (1,2). This statistic does not include disposal in designated landfills, but rather it applies to reclamation of marginal or drastically disturbed land as well as the use of sludge as a fertilizer for croplands.

As population and the degree of wastewater treatment sophistication increases, the quantity of sewage sludge produced by each community can be expected to multiply dramatically. Furthermore, economic and environmental pressures may shift the emphasis from presently preferred methods of disposal (ocean dumping 15%, landfill 25%, incineration 35%) to land application (2). Naturally, such a shift in emphasis will be accompanied by an increased demand for suitable land disposal sites (3). This problem is expected to reach critical proportions in certain localized areas (such as in the Northeastern U.S.) where large populations are confronted with a relative scarcity of farmland. In these areas, the disadvantages of land application -- lack of public acceptance, odors, pathogens (4,5,6), toxic metals (5,6,7), and the possible presence of industrial chemicals (5,9,10) -- will become greatly magnified. Concern over the fate of such pollutants in the soil and groundwater and their impacts on vegetation and the food chain is well placed and must be definitively answered in the future.

The purpose of this study was to investigate an electrochemical process for the removal of heavy metals directly from sewage sludge without prior dewatering. Sludge does contain macronutrients useful to plant growth (such as nitrogen, phosphorus and potassium) but it may also contain substantial quantities of metals, some of which (most notably Cd, Zn, Ni, Cu and Cr) have been found to be toxic to vegetation at elevated concentrations (1,5,11-13) and may accumulate in the human food chain (5,14,15). Concern over the migration of these elements into the food chain has resulted in the proliferation of many guidelines that recommend limits on the amount of sludge applied to farmland based on the amount and species of metal contaminants involved (5,16-20). The objective of the Union Carbide demetalization process is to reduce the concentrations of such metals sufficiently to allow an increase in the amount of sludge that may be applied to the available acreage.

## SECTION 2

## CONCLUSIONS

The sludge demetalization process was successful in removing metals from sewage sludge without prior dewatering. Copper, zinc, cadmium, nickel, chromium and (to a smaller extent) lead were removed from solution and accumulated on the electrodes. Unfortunately, the metal concentration reductions and the coulombic efficiency of the plating process were disappointingly low, resulting in projected treatment costs that were higher than most methods of sludge disposal currently in use. Furthermore, attempts to correlate metal removal performance with system operating parameters were largely unsuccessful. Thus many improvements and additional developmental work must be done before the process can be commercially successful. Other important conclusions developed as a result of this study are as follows:

1. The Cu-$CuSO_4$ reference electrode was a useful tool in controlling total cell voltage and thus, indirectly, current density. Operating voltages in the 2 to 3 volt range were observed at a reference voltage of -1.4 to -1.45 volts. Such potentials were shown to be capable of plating very electronegative ions (such as zinc) at lower potentials than the 3 to 4 total cell volts that were used when operating without the reference electrode.

2. The identification and elimination of possible sources of metal contamination in the reactor design was found to be a critical step in attaining reasonable metal removals and approaching a metal balance around the reactor.

3. Despite the elimination of possible metal contamination and a change in process fluid from sludge to synthetic metal ion solution, process performance remained below expectations. This suggests that obstacles to higher metal removals and coulombic efficiency lie in the electrodeposition process itself rather than in interferences from the sludge solids.

4. In both laboratory and bench-scale tests, flakes and particles of deposited metal can spall off the electrodes and remain suspended in the agitated electrolyte. This agitation is necessary to reduce the boundary layer thickness at the electrode surface and to enhance the transport of metal ion species from the bulk solution to that boundary layer. Thus some compromise must be made between the improvement of mass transport from bulk

agitation and the difficulty of recovering the spalled off metal that results. Bench-scale testing indicates that this resuspended material can account for up to 10% of the metal deposited on the electrodes.

5. Gas aeration plays a significant role in improving bulk agitation, but performance does not seem to be sensitive to the quantity of gas used within the range tested. Nitrogen or air seem to be interchangeable as the aeration gas.

6. Of those materials tested, aluminum is preferred for the cathode and graphite for the anode. Stainless steel was also tried out as a cathode material, but it was deemed unsuitable because of extensive corrosion at low voltages. Similarly, aluminum was found to be a poor anode, since it slowly dissolved into solution. A sulfated lead electrode with low solubility was also tried out as an anode material, but the deposits formed on the cathode during its use were less adherent than those experienced with graphite anodes under the same conditions.

7. Laboratory-scale tests revealed that deposits formed from cadmium solution were less adherent than those formed from a solution containing both cadmium and zinc ions. Furthermore, as metals plated out on the cathode, its surface area increased, resulting in an increase in current until the metal ions were depleted from solution.

8. In the bench-scale tests with sludge, the solution pH was initially dropped to the 3 to 4 range by the addition of 10N $H_2 SO_4$. During the course of the experimental runs, small amounts of acid solution often had to be added to maintain this low pH. Our hypothesis is that the reduction of metal ions at the cathode shifts the acid hydrolysis equilibrium, causing more $H^+$ ions to be consumed.

9. Sludge foam, when it did occur, was successfully suppressed, either through the addition of small amounts of antifoaming agent or by a flat-bladed impeller rotating in the gas space above the fluid.

## SECTION 3

## RECOMMENDATIONS

At present, the direct electrochemical treatment of sewage sludge does not seem to offer a practical means of metal removal. Since the removal of heavy metals from both municipal and industrial sludges is becoming increasingly critical in today's environment, and since alternatives are not plentiful, further investigation of the process to improve its performance may be warranted. The relatively weak metal removals and low coulombic efficiency of this process seem to be tied to the electrolytic cell performance rather than to any interference from the sludge. Thus future experiments should be undertaken to identify and eliminate these obstacles to improved performance.

SECTION 4

# BACKGROUND

## PROCESS DESCRIPTION

The need for an efficient method of removing heavy metals such as cadmium, chromium, copper, zinc, lead and others from municipal wastewater sludges has been made all the more pressing through the growth of land disposal of sludge in the United States. It is desirable to remove metals from sludge prior to land disposal since possible toxic effects and the resulting regulation of application rates are tied to the quantity of metals disposed of. If the metal concentration of the sludge is low, a greater quantity of material may be deposited on a given acre of land before disposal limits are reached. A method is required that reduces most ions of interest to some degree, since preferential removal of one or two metals simply shifts the controlling concentration to another species. The form in which the metals are removed from sludge is important, since the process must not trade one environmental threat for another. Furthermore, the chosen method of removal must accomplish these goals reliably and economically.

The Union Carbide sludge demetalization process is intended to provide just such a solution to the metal removal problem. This process, (illustrated in Figure 1 through 3) involves the direct electrowinning of metals from aerobically digested, acidified municipal sludge.

It has been found through work published by other authors (21-24) and confirmed through bench top experiment at Union Carbide's Tonawanda Laboratories that the bulk of metals contained in municipal sludge are locked in the solid rather than aqueous phase. These solid phase metals are held primarily in two forms: insoluble organometallic complexes (21) and insoluble hydroxide, carbonate or sulfide compounds. In order to effectively reduce the concentration of metals in sewage sludge, these metals must be liberated from the solid phase and allowed to dissolve in the aqueous phase.

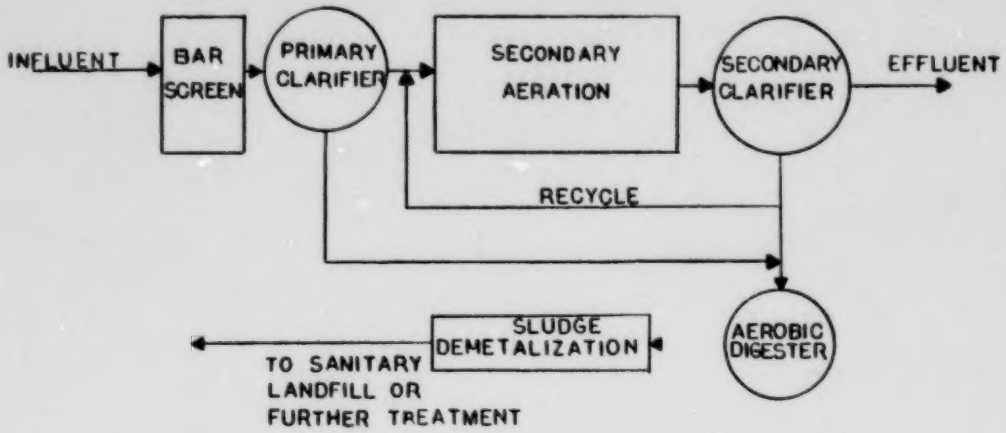


Figure 1 UCC Sludge Demetalization Overall Plant Flow Scheme

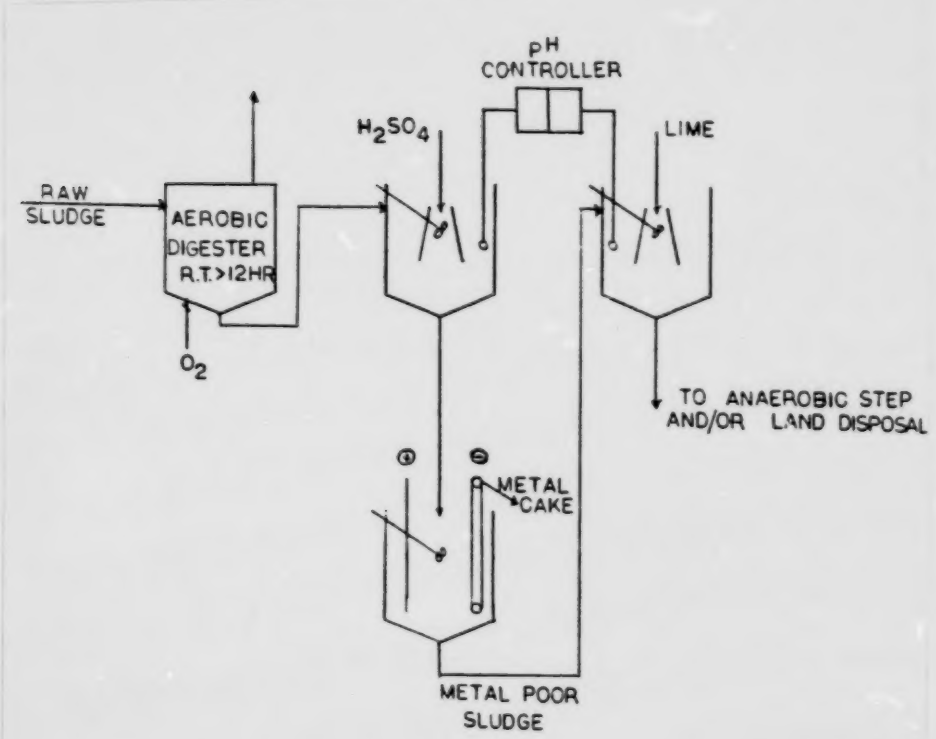


Figure 2 Electrochemical Metal Removal - Process Flow Schematic

## BASIC UNIT OPERATIONS

### (1) AEROBIC THERMOPHILIC DIGESTION

$$M - S + O_2 \xrightarrow[\text{Bacteria}]{\text{Aerobic}} M - SO_4 \longrightarrow M^{+2} + SO_4^{-2}$$

- Temperature 50-60°C
- Retention time 4-5 days
- High purity $O_2$ feed
- High solids concentration
- High shear aeration

### (2) ACID HYDROLYSIS

$$\log M_S = A + B \log M_1$$

- Acidify sludge to pH 4.0
- Prefer use of $H_2SO_4$
- Equilibration time 15 min.

### (3) ELECTROLYSIS REACTOR

- Operate above ambient temperature
- Stationary electrode system
- Recycle sludge flow
- Operating potential-1.5-2.0 volts vs. Cu - $CuSO_4$
- Aluminum cathode, graphite anode

### (4) NEUTRALIZATION

- Return pH to 6.5-7.5 range
- Prefer to use lime

Figure 3 Sludge Demetalization Design

The proposed sludge demetalization process accomplishes the solubilization of metal ions in sewage sludge through a pair of pretreatment steps. First, the sludge is aerobically digested to oxidize organic material and convert insoluble heavy metal sulfides to the soluble sulfate form via the following mechanism:

$$M\text{-}S + O_2 \underset{\text{aerobic}}{\rightleftharpoons} M\text{-}SO_4 \longrightarrow M^{+2} + SO_4^{-2} \quad (1)$$

Metal Sulfide — Oxygen — Bacteria — Metal Sulfate

The reason that metal sulfides rather than carbonate or hydroxide precipitates are a major concern is that in the pH range typical of wastewater sludge (6 to 8) the formation of the latter species is minimal. Experiments indicate that thermophilic (greater than 45°C) aerobic digestion with high purity oxygen for a period of one-day is sufficient to convert the metal sulfides to the soluble form. Figure 4 illustrates the effect which aeration time plays in the distribution of cadmium and nickel between the solid and liquid phases.

The second step involves a shift in the equilibrium which exists between the dissolved heavy metals and the insoluble metallic complexes contained in the sludge solid phase. This shift is produced by the addition of acid which lowers the pH of the solution and causes the displacement of metal ions by $H^+$ ions.

$$SI\begin{matrix}COO\\COO\end{matrix}M + 2H^+ \longrightarrow SI\begin{matrix}COOH\\COOH\end{matrix} + M^{+2} \quad (2)$$

sludge solids metal complex — sludge solids — metal ion

The extent of metal solubilization by this method is a function of the pH to which the sludge is acidified. Tables (1,2) and Figure (4), which were developed in the preliminary investigations of metals solubility, provide a quantitative feel for the sensitivity which the partition coefficent (defined as metals in solids/metals in solution) has to changes in $H^+$ ion concentration and will be explained in more detail later in this report. The shift in metal complex equilibrium occurs relatively rapidly upon acid addition, as illustrated by figure 5 which shows the effect which time since acid addition has on the cadmium levels

in the liquid and solid phases of the sludge. The increase in liquid phase cadmium concentration levels out after approximately 20 minutes.

It is at this point that the proposed demetalization process diverges from other published methods for metals removal from sludge which advocate the separation of the solid and liquid phases by a dewatering step followed by treatment of the liquid supernatant by chemical precipitation, electrolysis or a variety of other means. This approach is limited by the efficiency of sludge dewatering technology and by the virtue of the fact that after separation, no further metal transfer from the solid to the liquid phase may occur. The proposed sludge demetalization process advocates the continuous stripping of metal ions directly from the sludge in an electrolytic cell. This cell may consist of a series of parallel plates arranged into electrode pairs across which an electric potential is applied. A reference electrode situated in the bulk solution provides the set point for the control of the voltage applied across the electrodes. The positive electrode of each pair (the electron acceptor) is defined as the anode while the negative (electron donor) is known as the cathode. Aerated sludge is circulated between the plates to enhance mass transfer of metal ions from the bulk solution to the surface of the cathodes where they are removed via electrodeposition. The equilibrium between the solid and aqueous phase metal ion concentration acts to replenish the soluble metal concentration by releasing more metals from the solid phase. Thus, through the judicious choice of operating conditions for the electrolytic cell (voltage, pH, temperature) the metal species of interest may be substantially removed. After treatment with lime to neutralize its pH, the demetalization process provides a stabilized, pasteurized and metals depleted sludge for disposal. Furthermore, when the useful life of the cathodes have been reached they may be regenerated, sold as scrap or disposed of along with any metal concentrated deposits in an environmentally secure manner.

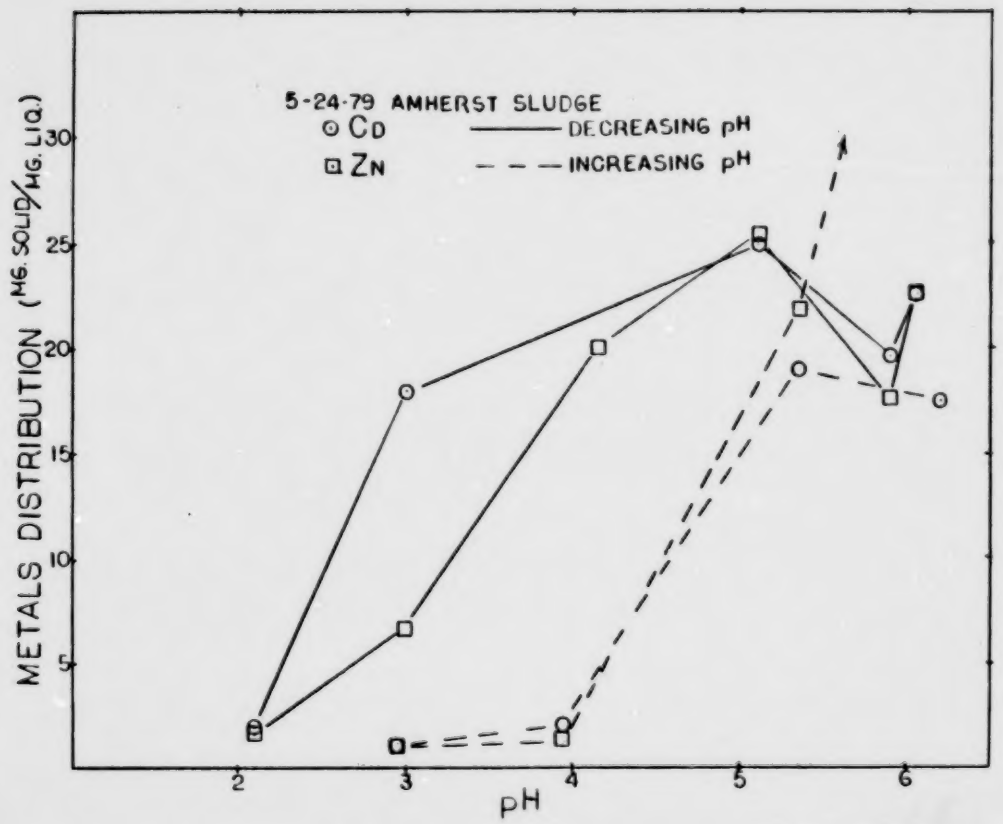


Figure 4 Metals Distribution versus pH

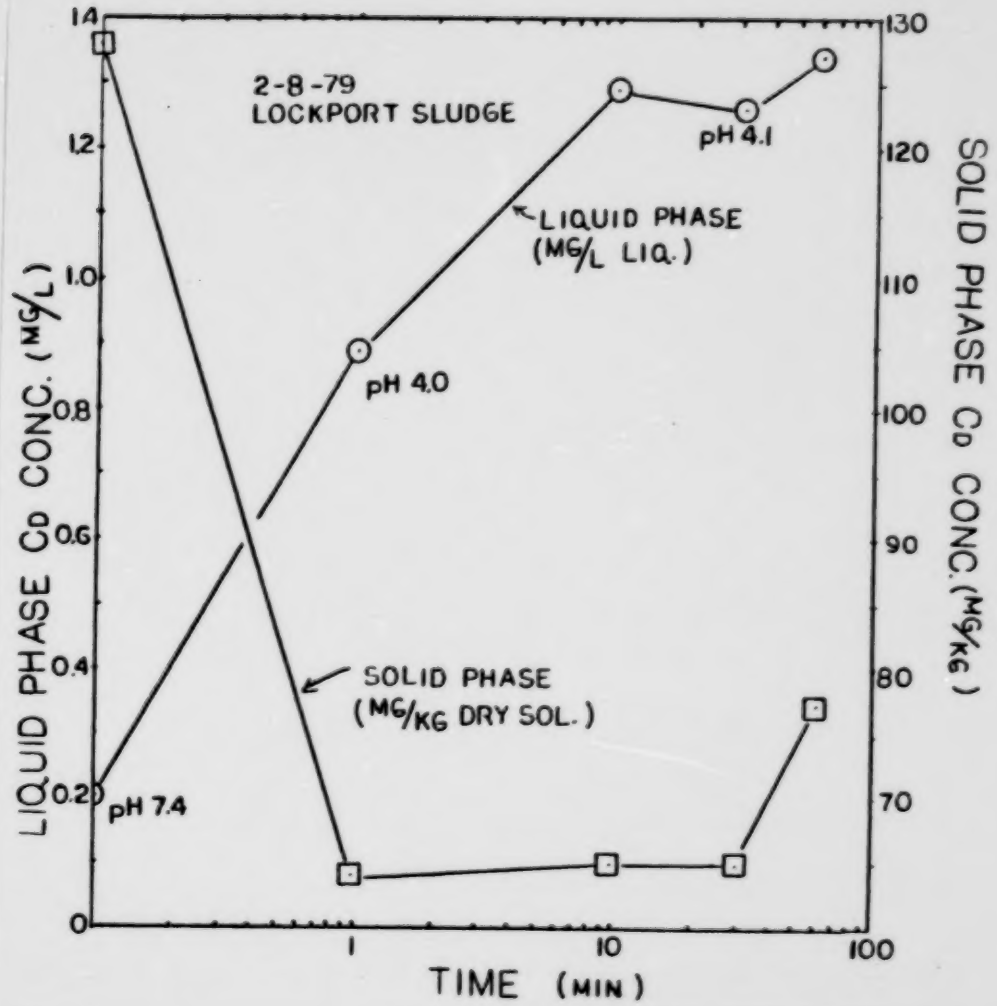


Figure 5 Cadmium Concentration versus Time of Acid Extraction

## AEROBIC DIGESTION

The thermophilic aerobic digestion of sludge has been previously treated in the wastewater literature (26-28). As mentioned before, the process involves the use of high purity oxygen or air to aerate thickened wastewater sludge and autothermally (without the use of an external heat source) raise the temperature to the thermophilic range (48-65°C). These temperatures are achieved and maintained through the oxidation of waste organic material resulting in a rapid stabilization of the digested sludge. A further benefit of operating in the thermophilic temperature range for periods greater than one day is the observed reduction in pathogenic organisms such such as bacteria, parasites and viruses (29,30). In addition to these results the digestion step also makes a contribution towards the solubilization of heavy metals. Although more has been written concerning the distribution of heavy metals in anaerobic sludges due to the ubiquitousness of that particular form of sludge treatment and its apparent sensitivity to toxic upsets, there has been evidence that aerobic digestion improves the solubility of heavy metals (31). Hayes, et. al. (24) state that "Variations in the chemical and biological characteristics of sewage sludges which define heavy metal distributions are also capable of producing some differences in heavy metal extractabilities between aerobic and anaerobic sludge upon acid treatment." They state that aerobically digested sludge has a higher oxidation-reduction potential (ORP) than raw or anaerobic sludges which allows a shift in the predominant metal ion species to a more soluble form when the pH is subsequently reduced below 4.0. An analysis is provided (figure 6) after the method of Hayes and Theis (22,24) for cadmium to illustrate this concept. As is evident from the diagram, increasing the oxidation/reduction potential at constant pH converts CdS to the more soluble $CdCO_3$ form. Reducing pH then increases the concentration of $Cd^{+2}$ in solution.

Past tests at Union Carbide's Tonawanda Laboratories indicate that aeration may cause a 25-40% increase in the quantity of heavy metals which may be extracted from sludge through acidification or chelation. In demetalization runs performed in our laboratory it was found (figure 7) that the concentration of insoluble Cd and Zn was reduced with increased time of aeration. Figure 8 shows that sludge digested for only 12 hours has the same first order reaction rate constant as sludge digested for 5 days. This indicates that only 12 hours of aeration at 50°C is needed to convert metals to the same available form as after 5 days digestion. The increased availability of metals indicated by figure 7 is verified by the electrolytic removal rate expressed in figure 8.

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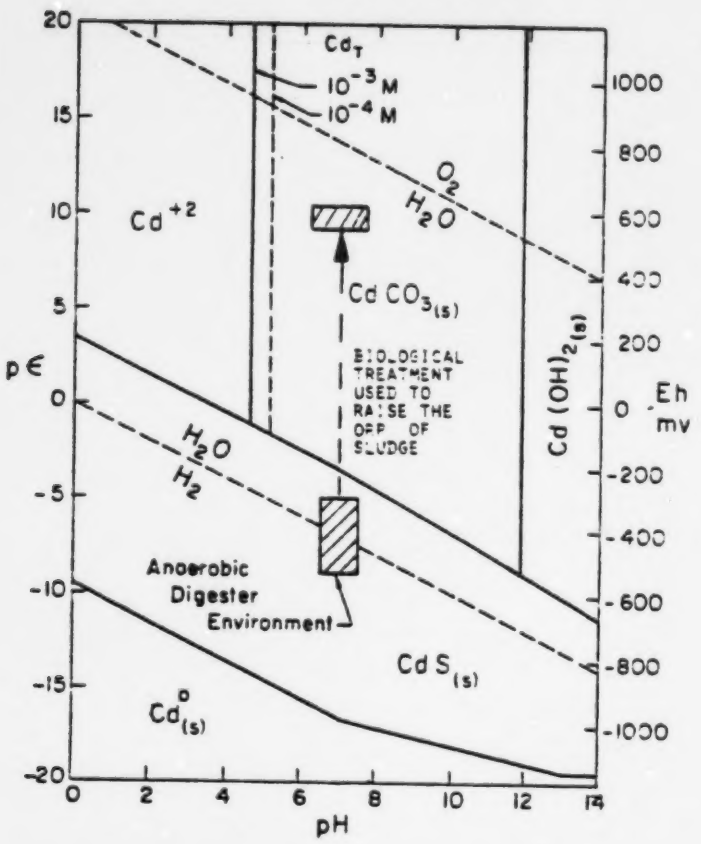



Figure 6 Predominance Area Diagram in Terms of pe Versus pH for Cadmium. Ligand Concentrations are $C_T = S_T = 10^{-2}$M; $P_T = 1^{-4}$M.

(reference 24)

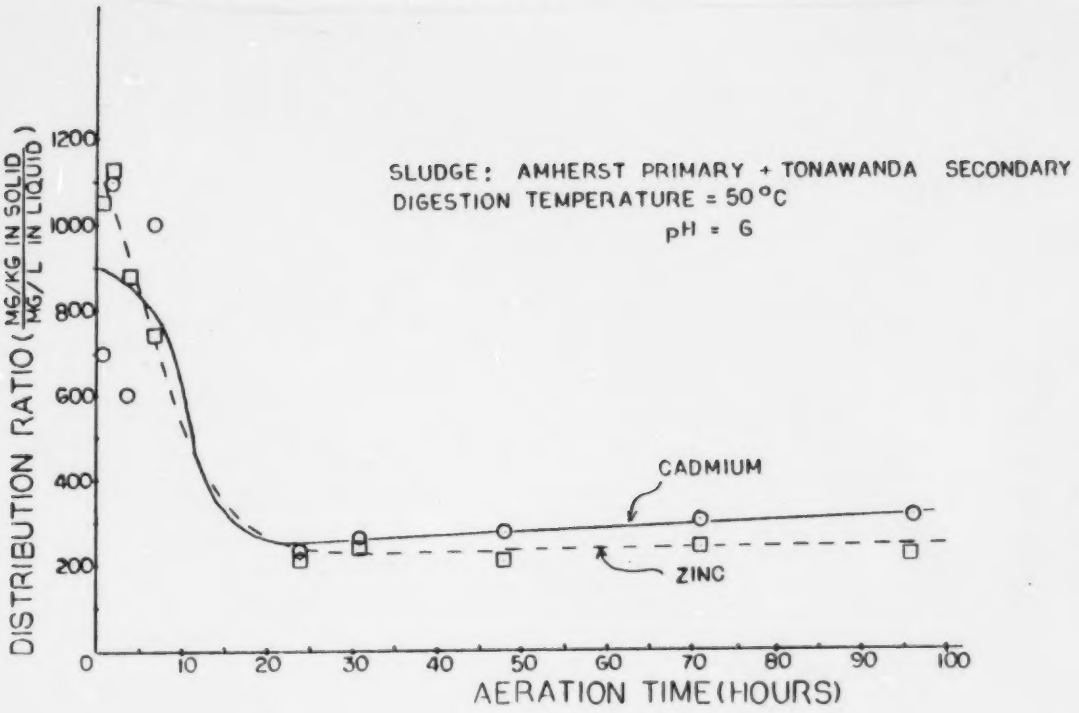



Figure 7 Effect of Aeration Time on Metals Distribution Ratio

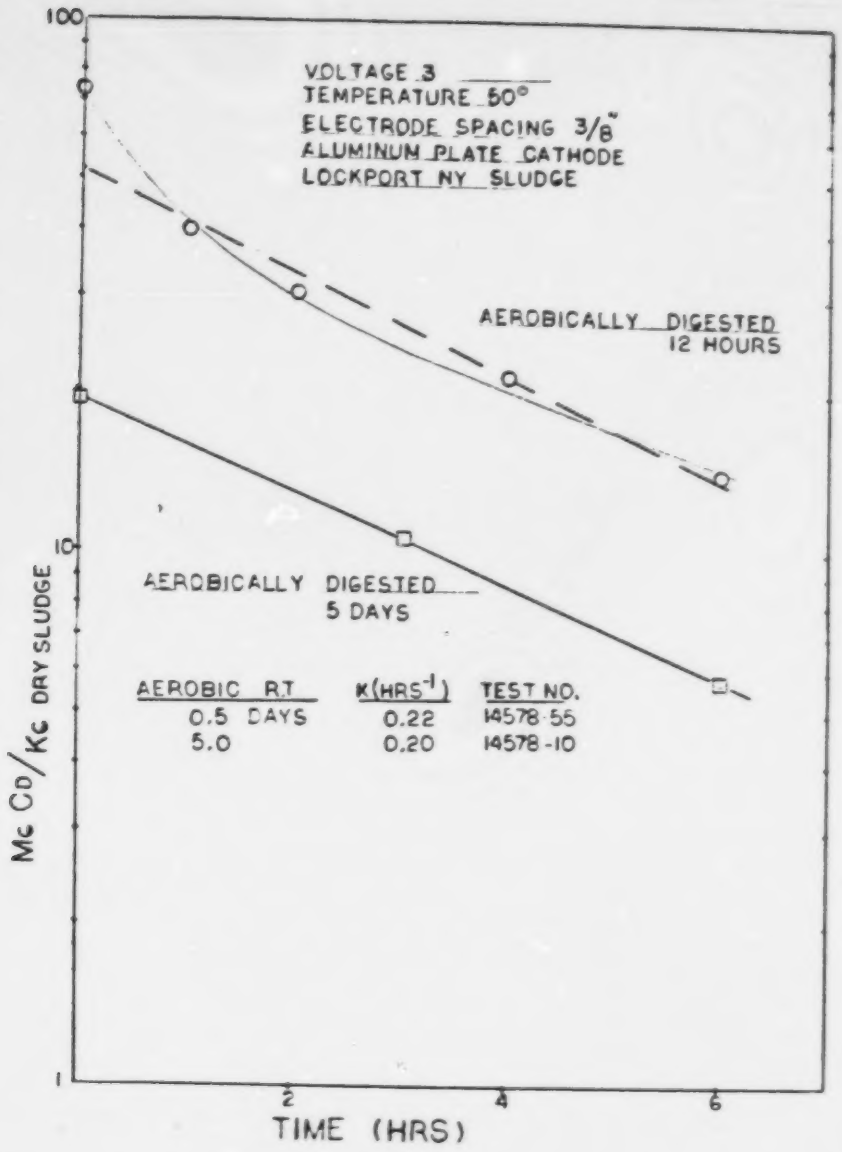



Figure 8 Cadmium Concentration versus Time of Batch Demetalization

## ACIDIFICATION

The importance of the role that sludge pH plays in the availability of heavy metals to soil or microorganisms has been discussed by numerous authors (12,13,18,21,22,34,35). The general agreement is that the lower the pH, the greater the mobilization of heavy metals from the solid to the liquid phase from which toxicity to plants or bacteria may occur. The relationship between pH and soluble metals concentration was experimentally verified at Tonawanda (Tables 1 and 2). In these tests the sludge sample was acidified to the desired pH, allowed to stand overnight, then centrifuged to separate the solid and liquid phases which were each analyzed for metals content. Results are given as the ratio of metals concentration in the solid phase to the metal concentrations in the liquid phase, termed the partition coefficent. As can be seen there is a substantial reduction in the partition coefficent at lower pH indicating a release of metals from the solid to liquid phase. In plotting the distribution of metals between the two sludge phases it was noted that the log of the metals concentration in the solid phase was proportional to the log of the metals concentration in the liquid phase (figure 9 and 10). Such a relationship implies a Freundlich-type adsorption model for the metals on the sludge solids as given by the expression:

$$\log M_S = A + B \log M_L \qquad (3)$$

where $M_S$ = metal concentration in solid phase
$M_L$ = metal concentration in liquid phase
A,B = constants dependent on pH

Subsequent to these results, tests were performed to determine the rate of metal solubilization upon acidification. In this test sludge samples were taken at various time intervals following the addition of acid to depress the pH. These samples were then centrifuged and the resulting phases analyzed for metal content. As figure 5 illustrates, the reaction reaches equilibrium within 10 minutes of acid addition. Also of importance, figure 4 indicates that the distribution ratio of metals in the solid phase to metals in the liquid phase drops sharply at a pH below 4.0. Furthermore the reversibility of the reaction was tested by adding alkali to sludge samples whose pH had previously been depressed with acid. A pH value of about 4 seems to be the breakpoint for both decreasing and increasing pH, but a hysteresis is present. This hysteresis is due to some lag time (greater than 15 minutes) which was the period between pH changes. Such a delay could be due to the hydrolysis of organic compounds that form metal complexes.

TABLE 1

Partition Coefficients for Metals at Different pH Values

| | pH 2 | pH 4 | pH 6 |
|---|---|---|---|
| Ag | 5 | 25 | 40 |
| Al | 3.9 | 350 | 600 |
| Co | 67 | 250 | 1000 |
| Cu | 20 | 100 | 240 |
| Fe | 0.4 | 1.1 | 3.2 |
| Mn | 1.7 | 3.3 | 20 |
| Mo | 3.3 | 4.5 | 11.4 |
| Ni | 2 | 10 | 20 |
| Pb | 3 | 20 | 40 |
| Zn | 2 | 150 | 200 |

TABLE 2

Effect of pH and Chelating Agents on Distribution of Metals Between Liquid and Sludge Phases of Slurry

(Expressed as mg/l)

| Treatment | Copper | | Cadmium | | Nickel | | Zinc | |
|---|---|---|---|---|---|---|---|---|
| | Liquid | Sludge | Liquid | Sludge | Liquid | Sludge | Liquid | Sludge |
| No treatment (pH6) | 13 | 143 | 0.05 | 0.35 | 27 | 65 | 83 | 478 |
| pH2 | 113 | 58 | 0.38 | 0.13 | 114 | 18 | 524 | 81 |
| pH3 | 61 | 101 | 0.37 | 0.18 | 97 | 27 | 451 | 128 |
| pH4 | 23 | 142 | 0.20 | 0.26 | 62 | 38 | 313 | 261 |
| pH5 | 12 | 152 | 0.09 | 0.33 | 14 | 50 | 172 | 380 |
| pH7 | 16 | 146 | 0.03 | 0.36 | 20 | 74 | 43 | 495 |
| pH8 | 30 | 127 | 0.02 | 0.37 | 13 | 80 | 26 | 525 |

(These partition coefficients are the ratios of all forms of the metals in the solid phase to all forms in the liquid phase.)

$$\frac{\text{mg metals/dry kg solid}}{\text{mg metals/ l liquid}}$$

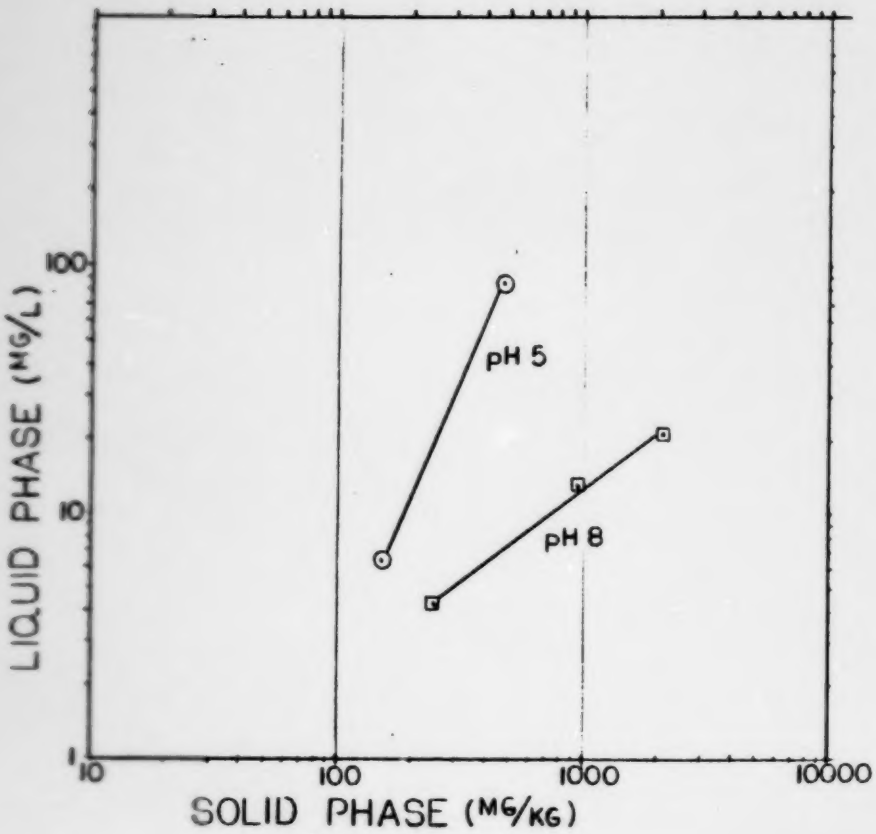



Figure 9 Effect of pH on the Distribution of Ni Between the Solid and Liquid Phases of Aerobic Thermophilically Digested Sludge

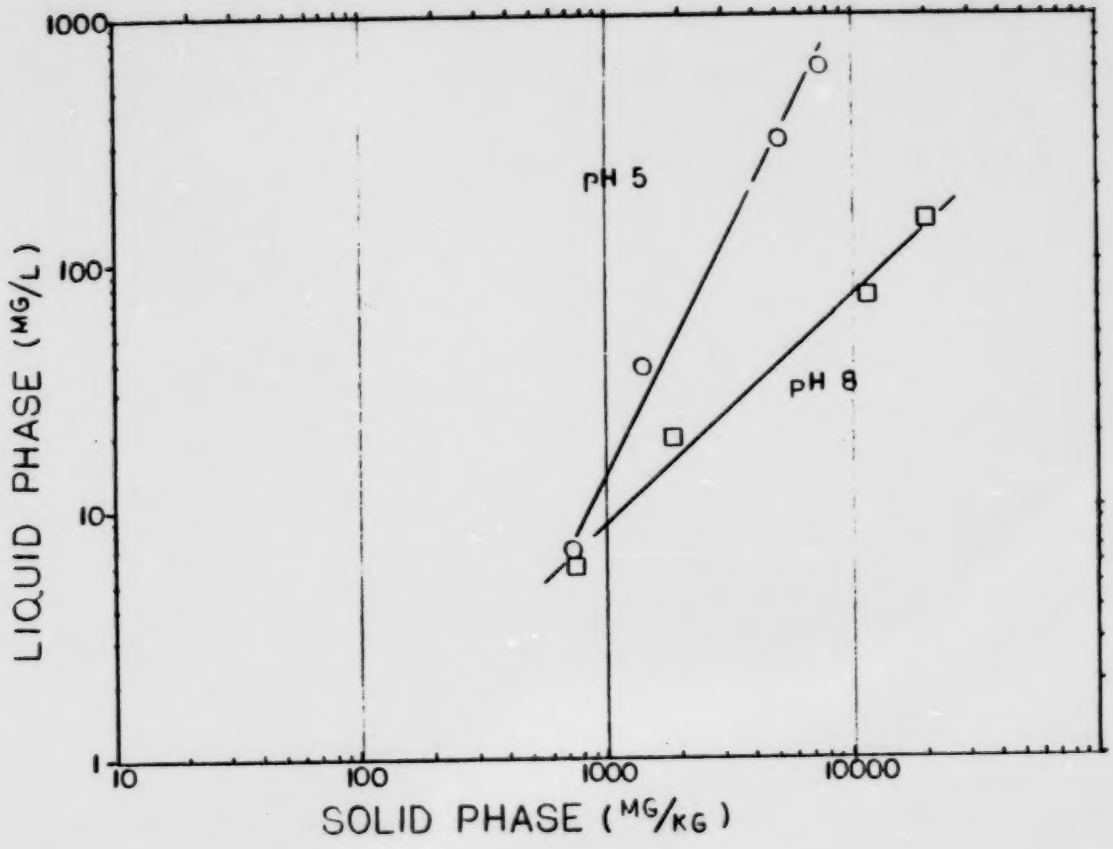



Figure 10 Effect of pH on the Distribution of Zn Between the Solid and Liquid Phases of Thermophilically Digested Sludge

## ELECTRODEPOSITION

At the heart of the sludge demetalization process lies the electrolytic cell. It is within this cell that metals are removed from the sludge and their charges neutralized. Although the mechanism of metal release by acid hydrolysis and the design requirements of autothermal thermophilic aerobic digestion are established technologies, the fundamentals of direct electrodeposition of metal ions from sewage sludge require development. Because of the importance of this subject to the proposed process a brief review is in order.

An electrolytic cell (shown in figure 11) consists of a pair of electrodes one of which is positively charged (anode) and the other negatively charged (cathode). These are immersed in a conducting medium, called the electrolyte, which carries a current from the anode to the cathode by means of positive and negative ions. As the ions reach the electrodes their charges are neutralized and the products of the electrolysis are formed. In the reaction of interest soluble metal ions are attracted to the cathode surface where their positive charge is neutralized and they plate out of solution. In order for the cell to function an electromotive driving force (voltage) must be applied across the cells and electrons must flow between them (current). The amount of current required depends on the rate of metals removal and the efficiency of the plating process ($\eta$). At 100% plating efficiency one gram equivalent weight of ions will be discharged at the cathode by one faraday, which is equivalent to 96,487 coulombs or ampere-seconds. One gram equivalent weight of a metal equals one gram atomic weight divided by its valence (the number of charges the ion carries). Thus the quantity of metal ion plated on a cathode may be expressed as:

$$\frac{\text{gram atomic weight}}{\text{valence}} \times \frac{\text{ampere - seconds}}{96{,}487} \times \frac{\eta}{100} = \text{grams metal deposited} \qquad (4)$$

The voltage between the two electrodes that the cell must operate at to achieve plating is dependent on several factors. The reactivity of the metal ion to be plated is of primary importance to the voltage selection. Table 3 from reference (36) presents experimental values for the equilibrium potential for many metal species. This is the potential, in volts, between the cathode and solution, as measured by the standard hydrogen electrode (SHE), when the metal is in equilibrium with the metallic ions at unit activity. These potentials are measured under conditions of zero current flow with specific quantities of dissolved salt present in the solution at 25°C and 1 atmosphere pressure in order to obtain comparable values. The hydrogen reaction is taken as a reference point so its equilibrium potential is set equal to zero. Ions which have a greater positive potential than hydrogen are more reactive than the $H^+$

ion and thus plate out more readily. For the negative values the cathode potential must be below the standard hydrogen potential by at least as many volts as the equilibrium potential for electrodeposition of that particular ion to occur. As the cathode is driven to progressively more negative values the metals should plate out according to the order shown in the table. Thus, for example, to plate zinc the cathode must be -0.762 volts with respect to the hydrogen electrode. At this potential all the metals higher in the table should be electroplated but $Mn^{+2}$ and $Al^{+2}$ will not plate since their potentials are lower. In actual practice the deposition potential required for metal ions removal may differ significantly from the values presented in table 3. Contributing to this difference are the concentrations of metal ions and temperature. These factors are related to the actual reduction potential through the well known Nernst equation:

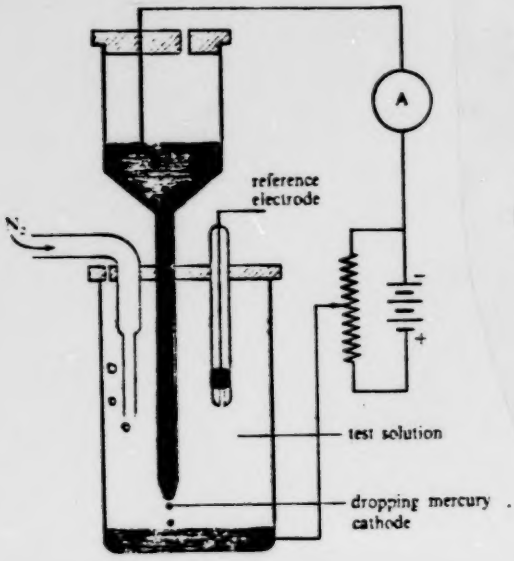
$$E = Eo + RT/nF \ln Ai \qquad (5)$$

where: $E$ = reduction potential (volts)
$E_o$ = equilibrium potential of the metal-metal ion couple (volts)
$R$ = gas constant (8.312 joules/degree K)
$T$ = temperature in degrees K
$n$ = number of gram-equivalents per gram-mole
$F$ = Faradays constant 96,487 coulombs/gram-mole
$A_i$ = activity of species i, which is approximately the concentration of the ion in solution.

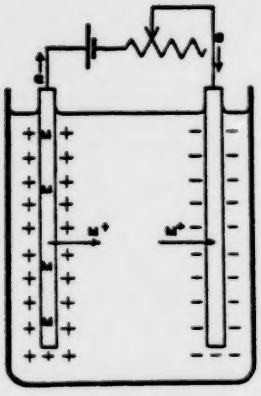
Considering the differences in electrode potential at 25°C (298°K) and 50°C (323°K), probably little difference in E would be noticed at thermophilic temperatures (323/298 = 1.08). Although the diffusion rate of metal ions also increases with temperature, if adequate turbulence is provided to the electrolyte through agitation, little mass transfer enhancement would be expected. The importance of these elevated temperatures is thus relegated to its role in the aerobic digestion pre-treatment step. That this is so has been borne out by experimental observations at room temperature and 50°C (25).

The effect which changes in metal ion activity (concentration) has on the electrodeposition potential is also small. Due to the logarithmic term in equation 5 large changes in $a_i$ produce only slight changes in E. Thus for all reasonable metal ion concentrations E will be close to $E_o$.

Figure 12 presents an illustrative example of a current-potential curve for a single metal ion species in an aqueous solution (36). The reduction potential E is shown as point E on the curve. As the reduction potential of the metal-metal ion couple is exceeded the current increases until point D is reached on the curve. This is the point at which deposition actually takes place at the cathode. The difference in voltage between points E and D on the curve is known as overvoltage and is a




Dropping Mercury



Solid Electrode

Figure 11 Typical Electrochemical Cells

Table 3 Electrochemical Potential Series
Standard Reduction Potentials Relative to SHE

| *Ion* | *Voltage* |
|---|---|
| $Au^{+}$ | +1.5 |
| $Ag^{+}$ | +0.7995 |
| $Cu^{+}$ | +0.0528 |
| $Sn^{++++}$ | +0.003 |
| $H^{+}$ | 0 |
| $Pb^{++}$ | −0.1264 |
| $Sn^{++}$ | −0.1406 |
| $Ni^{++}$ | −0.231 |
| $In^{+}$ | −0.336 |
| $Cd^{++}$ | −0.4024 |
| $Cr^{+++}$ | −0.509 |
| $Zn^{++}$ | −0.762 |
| $Na^{+}$ | −2.7125 |

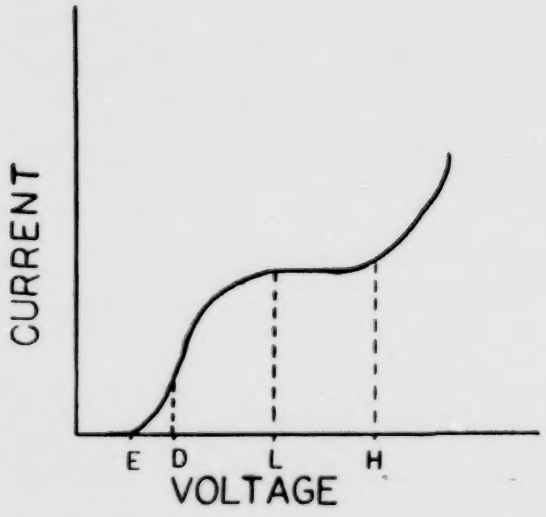



Figure 12 Current-Potential Curve

function of the resistance to current flow in the electrolytic solution. More will be discussed later on this subject. Further increases in voltage above D cause increased deposition to occur and the current will rise until point L is reached where the current-potential curve levels off. At this point the metal ions are discharged as fast as they are brought up to the cathode surface by diffusion. The current at point L is known as thediffusion current while the potential will correspond to the value given by the Nernst equation for a very small value of the activity (Ai) which represents the concentration at the electrode surface. Although the bulk solution may have a much higher activity, the concentration at the cathode surface is still limited by diffusion across a thin (~50-100 μm) boundary layer between the solution and the electrode. Under normal conditions the plating current cannot exceed the diffusion current even if the solution is strongly mixed. The diffusion current is proportional to the bulk concentation of metallic cations. Thus in an efficient electroplating process the cathode potential will be increased (negatively) until the diffusion current corresponding to the most difficult to remove element is attained. Further increases in potential will not increase the plating current and may contribute to unwanted reactions and losses resulting in a decrease in plating efficiency. An example of such an unwanted cathode reaction is the rapid evolution of gaseous hydrogen which occurs as a result of the dissociation of water as the potential is increased above point H in figure 12 and the hydrogen overvoltage is exceeded. The point at which this occurs (equilibrium potential = -0.828v versus SHE) represents a practical upper limit of cathode potential in an aqueous solution.

The substantial overvoltage needed to discharge hydrogen gas at the cathode is a fortunate occurence. Referring to table 3 once again, it can be seen that most of the metals of interest have equilibrium potentials more negative than that of the hydrogen reaction. Therefore in aqueous acid solutions one might expect the evolution of hydrogen gas to be performed in preference to many of the metal - metallic ion couples. If this were to occur, the plating of such metals as zinc (reduction potential of -0.763v versus SHE) would be difficult if not impossible. Fortunately the deposition voltage for zinc and most of the metals is sufficiently low that the metals plate out on the cathode before the hydrogen voltage is exceeded.

Actual plating conditions are not ideal and dynamic conditions in the electrolytic cell (mass transfer, electrode film resistance) set up a force or reverse potential in the cell which acts against the flow of ions. This force can be measured as a voltage and is the overvoltage described previously. If the deposition voltage of the $Zn^+$ ion exceeds the hydrogen overvoltage, hydrogen gas will evolve exclusive of Zn. However the overvoltage, for the reduction of $H^+$ to $H_2$ is quite large since hydrogen evolution is impeded by a slow reaction rate on most electrode materials. As the current density of an electrolytic cell (expressed as amps/unit area of cathode) increases, the extent of polarization at the electrodes increases, thus favoring metal-metal ion

complexes which are more negative on the equilibrium potential scale. This accounts for the experimental observation that although some $H^+$ ions are reduced to $H_2$ (causing a slight increase in pH), there is substantial removal of metal-metal ion complexes which are more electronegative than the $H^+$ reaction.

There are three identifiable sources of overvoltage: activation, ohmic and diffusion overvoltage. Activation overvoltage is due to an irreversible reaction occurring on the electrode suface. Ohmic overvoltage (also called iR voltage drop) is due to the solution resistance to current flow. Diffusion overvoltage (also called concentration overvoltage) is the product of limitations of the mass transfer of reacting species from the bulk solution to the electrode surface. The overall potential (or total cell voltage) is a combination of the reversible potential and the sum of these various voltage losses as given by the expression:

$$V = E + \eta_A + \eta_D + \eta_O \qquad (6)$$

where $V$ = total cell voltage
$E$ = reduction potential
$\eta_A$ = activation overvoltage
$\eta_D$ = diffusion overvoltage
$\eta_O$ = ohmic overvoltage

These various overvoltages are a function of current density, electrolyte characteristics and cell operating parameters as shown by the following equations.

$$\eta_A = a + b \ln i \text{ (Tafel Equation)} \qquad (7)$$

$$\eta_O = iR \text{ (Ohms Law)}$$

$$\eta_D = \text{function of } (T, n, dc/dx) \text{ (From Fick's Second Law)}$$

where:
- $a, b$ - constants
- $i$ - current
- $R$ - solution resistance = $1/k \; d/A$
- $K$ - sludge conductivity
- $d$ - distance between electrodes
- $A$ - area of cathode
- $n$ - number of equivalents per mole
- $dc/dx$ - concentration gradients
- $T$ - absolute temperature

Experimentally, the study of current-potential curves for electrolytic solutions is performed by varying the current and measuring the voltage and is known as polarography. For an electrolytic solution consisting of several different metal ion species, the polarograms show a sequence of sigmoidal waves (figure 13) which appear as steps. The center

of each step is the "half-wave potential" for the particular ion being reduced at that voltage. The plateaus are the sums of diffusion currents which are proportional to the concentrations of the ions being reduced. The polarogram is thus the electrochemical spectrum of the ions in the solution and may be used to determine the identity and concentration of reducible ions.

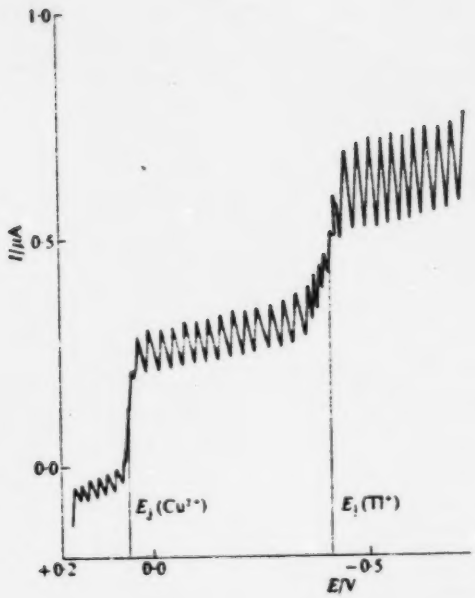



Figure 13 A Polarograph Indicating the Presence of $Cu^{+2}$ and $Tl^{+}$ ions

## NEUTRALIZATION

Since the sludge is acidified to a pH of about 3 to remove the metals, in order to comply with land disposal regulations and to prevent acid damage to crops, the demetalized sludge must be neutralized to a pH of 6.5-8.0. This is accomplished through the addition of an alkaline agent (such as lime) to restore the original balance between $H^+$ and $OH^-$ ions as well as the buffering capacity of the sludge. Such alkalinity addition also serves to immobilize any solubilized metals remaining, forming insoluble metal precipitates which, if soil pH is maintained, are not expected to enter the food chain.

Many treatment plants provide for sludge dewatering prior to land disposal. Where such dewatering is necessary it is interesting to note that short term acidification of sludge enhances dewatering characteristics (24) with results comparable to conventional aids such as ferric chloride or polymers. In such cases dewatering step could take place prior to neutralization resulting in a conditioned sludge ready for disposal and a metals containing supernatant which may be treated separately with lime to form an inorganic metal precipitate or recycled in untreated form to the head of the works or perhaps used as electrode rinse water. Any lime sludge resulting from the treatment of supernatant could be disposed of separately from the organic sludge.

SECTION 5

# LABORATORY TESTS

## OBJECTIVES

It was desired to study electrode and cell operating conditions on a small scale apparatus considering only electrochemical variables without the uncertainties attendant to wastewater sludge. Dropping mercury electrode tests were performed to determine the potential with respect to various reference electrodes at which the ions of interest will reduce to the metallic state. Polarograms or current versus applied potential plots were generated in order to measure hydrogen overvoltage, the degree of oxygen interference and the behavior of metal ion deposition in weak sulfuric acid solution. These results can then be used to establish minimum power levels of electrochemical reactions. The cathode potential is measured and controlled with respect to the electrolytic solution. It must be sufficiently negative to remove the ions of interest yet it must not be so negative that an appreciable amount of hydrogen is formed.

Solid electrode tests were also run in the laboratory for the purpose of finding suitable combinations of cathode, anode and reference electrode materials. These tests were also used to study the reduction and plating of metal ions from solution under controlled potential electrodeposition and the factors which may influence the metal removal rate and coulombic efficiency.

## EXPERIMENTAL APPARATUS AND PROCEDURES

Stock sample solutions were prepared containing 10-100ppm each of Cadmium, Zinc, Copper and other metals in varying combination. The pH of these aqueous solutions was depressed by the addition of $H_2SO_4$ and then deaeration achieved through agitation with nitrogen. In some instances suppressants such as methyl-red or gelatin were added as maxima suppressants or to simulate the effect which organic matter might have on the shape of the current potential curves. These sample solutions were placed in 40 ml dropping mercury electrode cell in order to obtain current-potential relationships for the various metal ions being investigated. The apparatus consisted of an Aardvark potentiostat,

potential scanner, current integrator, a reference electrode system and various pieces of recording equipment. The cell can be used with either a dropping mercury cathode or a stationary electrode.

The various pieces of equipment used include:

- AIS Systems of Floyd Bell Associates (Aardvark)
  V-2LR-D Digital Potentiostat
  Scan 4 Scanner
  MSA Microscan Attachment
  X-Y 815 Recorder 11" x 17"

- Alpha Research Company
  Model 701 Integrating Coulometer

- Princeton Applied Research
  Corrosion Cell (Figure 14)
  G-101 Storage Battle for Bridge Tubes
  G-0023 Dropping Mercury Electrode Kit
  G-0093 Mercurous Sulfate Reference Electrode

Polarographic tests were conducted by varying the potential and measuring the current which results from the reactions at the electrodes. The solution pH, metal ion species and concentration were varied between test runs and the results recorded as in figure 13 as a series of sigmoidal waves each representing a different reaction. Reference electrodes determine the potential between the working electrode (or cathode) and the electrolyte while potentiostats, control this potential during the course of a test. Only a very small current is tolerated between the working and reference electrodes.

Samples were analyzed by Union Carbide's Analytical Services Laboratory at Tonawanda. Electrodes and electrolyte were analyzed for Cu, Zn, Pb, Ni, Cd, Cr. Electrodes were washed with a solution of nitric acid and the quantity of metals in the resulting solution determined via atomic absorption. A microprocessor was used to analyze absorption data and determine the metal species.

## RESULTS

Small scale tests were conducted in order to make controlled electrochemical measurements of electrode potentials and to investigate the conditions required for metal deposition and the nature of the electrode reactions. Particular attention has been paid to determining the extent to which unwanted side reactions, such as the reduction of $O_2$ to $OH^-$ in acid solution or $Cr^{+3}$ to $Cr^{+2}$, reduce the coulombic efficiency of the demetalization process. In addition a different method of electrochemical reactor control was explored, namely "controlled potential electrolysis".

## Polarographic Reduction Spectrum

In these experiments the actual half-wave potentials of metals in sludge/acid solution were determined. Due to the possibility of chemical complexation these could be very different from the reference values of table 3. These wave potentials are dependent on the chemical nature of the electrolyte and may also be dependent on the electrode material. To this end, the reduction potentials for $Cu^{+2}$, $Pb^{+2}$, $Cd^{+2}$, $Fe^{+2}$ and $Pb^{+2}$ have been calculated as a function of concentration by solving the Nernst equation using the standard reduction potential for each ion. The metals should plate out of solution in the order given by table 3 but if the ion is complexed in the solution it will have a more negative reduction potential.

In order to obtain the current-potential curves or "polarograms" for the reactions of interest the dropping mercury electrode apparatus was constructed. Tests were performed with dilute aqueous solutions of the metal sulfates adjusted to a pH of 4.0 with sulfuric acid. Dilute solutions ($10^{-5}$ - $10^{-2}$M) of $Cu^{+2}$, $Cd^{+2}$ and $Zn^{+2}$ were studied extensively with some additional tests of $Ni^{+2}$, $Cr^{+2}$ and $Fe^{+2}$ solutions. No additional supporting electrolyte was used except where noted in comparison tests. A substantial number of polarograms were run to determine the effects of different ionic strengths and additives. For details see appendix A. The following observations were made:

(1) The recorded polarograms were of the shape anticipated. At low potentials the currents were low until the reduction potential was approached. The current then rose in a sigmoidal wave and reached a plateau level. This level remained reasonably flat until the next reduction wave or until $H_2$ evolution occurred. The shape of a typical test polarogram is illustrated by figure 13.

(2) The measured half-wave potentials of $Cu^{+2}$, $Cd^{+2}$ and $Zn^{+2}$ were close to the values of the standard reduction potentials calculated for these ions with respect to the $HgSO_4$, $Hg_2Cl_2$ and $CuSO_4$ reference electrodes. Note that the reference electrode carries no appreciable current and thus should not be disturbed by the many current-dependent overvoltage effects. Virtually all of the electroplating current passes through the anode.

(3) The reductions of $Cr^{+3}$, $Ni^{+2}$ and $Fe^{+2}$ were considerably more cathodic than their standard reduction potentials. $Cr^{+3}$ gave a broad wave between $Cd^{+2}$ and $Zn^{+2}$ while $Ni^{+2}$ gave a very broad wave more cathodic than $Zn^{+2}$. With $Fe^{+2}$, a wave could just be observed superimposed on the final hydrogen wave. It is therefore not feasible to plate iron under these conditions, however nickel removal may be feasible at cathode potentials more negative than those required for $Zn^{+2}$.

(4) The hydrogen gas evolution wave was observed at approximately -2.1 volts indicating that this is not a major competing reaction for metals removal under these conditions. With mercury or $CuSO_4$ cathodes, $Zn^{+2}$ and all the more electronegative ions may be electroplated without great interference from $H_2$ evolution.

(5) The $Zn^{+2}$ ion (the most difficult to reduce based on table (3)) can be reduced to concentrations of $\sim 10^{-7}$ eq./l by the following potential/reference electrode combinations:

| Potential | Reference Electrode |
|---|---|
| -1.00 | normal hydrogen electrode |
| -1.25 | saturated $Hg_2Cl_2$ (calomel) |
| -1.32 | saturated $CuSO_4$ |
| -1.64 | saturated $Hg_2SO_4$ |

The concentrations of metal ions more electronegative than $Zn^{+2}$ would be expected to be reduced to even lower levels under these conditions.

(6) In aerated solutions small waves around -0.3 volts and -0.8 volts were observed and attributed to the reduction of oxygen since they disappeared upon deaeration with nitrogen gas.

(7) Large "maxima" were observed with $Cu^{+2}$ and smaller "maxima" with $Zn^{+2}$. These interferences are reduced by the addition of small concentrations of gelatin, without appreciably shifting the waves. However, the addition of a silicone-based anti-foam agent did shift the waves in a cathodic direction. Added $Cl^-$ ions shifted waves recorded with $Hg_2SO_4$ reference electrodes in an anodic direction, probably due to calomel ($Hg_2Cl_2$) formation.

(8) In dropping mercury electrode cells a concentration gradient is formed resulting from the depletion of ions at the electrode surface by the electrode reaction. At the limiting current the ion is reduced (or oxidized) as rapidly as it reaches the electrode surface and its concentration at the electrode surface reaches a steady-state value which is negligibly small compared to the concentration in the bulk solution. Under such conditions the current is nearly independent of applied potential and is governed solely by the supply of ions to the electrode surface. The limiting current is made up of two components a "diffusion" current and a "migration" current. The first is a driving gradient at the electrode surface while the second is force which is proportional to the electrical potential difference between the electrode surface and bulk solution.

The limiting currents in the electrolyte used for these tests (metal ions in a dilute sulfuric acid solution) appear to be "migration" rather than "diffusion" currents. This was demonstrated by adding large

amounts of the salt $K_2 SO_4$ to the relatively dilute solution of metallic ions. This makes the migration of charges much easier and practically eliminates the migration portion of the limiting current. In this experiment the limiting (diffusion) currents were then half as large as those before salt addition. For $10^{-3}$M solutions, the measured migration currents correspond to a current density of about 2 amperes per square meter of cathode surface.

The major conclusion of this test series is that the best cathode potential for controlled potential deposition is approximated -1.45 volts versus the $Cu\text{-}CuSO_4$ reference electrode. This voltage should sufficiently reduce the $Zn^{+2}$ concentration below $10^{-8}$ M and effectively take more electronegative metals to even lower concentrations. A more detailed examination of dropping mercury electrode test results may be made by referring to Appendix A.

Electrochemical Cell Experiments - Electrode Tests

In previous laboratory tests a dropping mercury electrode was used to determine the potentials at which the various ions of interest will plate out of solution. In the next series of experiments detailed in appendix B attention was shifted to the reduction and plating of metals on solid cathodes. Initial exploratory tests were made with 3003-F Aluminum and various steel cathodes plating $Cd^{+2}$ and $Zn^{+2}$ ions at a pH of 4. Multiple potentiometric scans showed a distinct wave and plateau corresponding to the reduction of $Cd^{+2}$ to Cd followed by a current rise, probably due to $H_2$ evolution. On increasing the applied potential in the positive direction a peak corresponding to the stripping of Cd from the cathode was observed at a potential somewhat below the reduction potential. The aluminum cathodes appeared to behave satisfactorily but with the steel cathodes a substantial anodic current was observed at potentials below about -0.7 volts versus the $Cu/CuSO_4$ reference, due to the corrosion of iron. Iron or steel is therefore not a satisfactory cathode material.

Potentiometric scans of $Cd^{+2}$ and $Zn^{+2}$ solutions at a pH of 4 with 3003-F Aluminum cathodes produced curves with well defined decomposition potentials corresponding to the reduction of each ion. The measured decomposition potential of $8 \times 10^{-4}$ M $Cd^{+2}$ was - 0.82 volts, and that of $1.8 \times 10^{-3}$M $Zn^{+2}$ was -1.13 volts, relative to the $Cu/CuSO_4$ reference electrode. These values agree well with the values calculated from the standard reduction potentials by the Nernst equation. On the same scale the current rise due to $H_2$ evolution occurred around -1.60 volts. This data confirms that a controlled potential of -1.4 volts is appropriate for plating out these ions in an Al cathode, $Cu/CuSO_4$ reference electrode system.

Graphite anodes were used extensively in these experimental runs. The anodic reactions which occur seem to consist of the formation of $O_2$ and $H^+$ ions. The solution was observed to darken as plating progressed due to partial dissolution of the graphite. Although this in itself does not represent an undesirable situation another, more stable, material might prolong the life of the cell. Since the cost of using a noble metal as a cathode material would be prohibitive the use of either an aluminum or sulfated lead anode was tested as an alternative to graphite. Although both materials appeared to function satisfactorily they both have their drawbacks. The aluminum anode exhibited areas of highly promoted general attack and crevicing at its surface. The sulfated lead anode tests were marked by very poor mechanical adherence of metallic deposits on the aluminum cathode. The rate of metals removal was also poorer for the lead anode.

Electrochemical Cell Experiments - Plating Studies

Solid electrode plating studies were initiated using a one liter test apparatus manufactured by Princeton Applied Research (Appendix C). The test solutions contained, nominally, 100 ppm levels of cadmium and zinc adjusted to pH4 with dilute sulfuric acid. All the solutions were deaerated during testing with nitrogen and stirred using a teflon coated magnetic stirrer. The surface area of the aluminum cathodes was 5.0 sq. cm. The anodes (2) were high density graphite rods. The open circuit potential of the aluminum, in this environment, was -0.76 volts versus $Cu/CuSO_4$.

The previous polarographic tests on $10^{-3}$M $Cd^{++}$ and $Zn^{++}$ solutions had indicated that the diffusion current density was about 2 amperes per square meter. Comparable current densities with the solid Al cathodes were anticipated, depending on the rate of stirring or agitation of the solution. As plating progressed, decreasing currents were expected due to depletion of the metal concentration in the solution. The measured currents in the plating studies were initially in the range expected and were increased by greater stirring. As the electrolysis proceeded, the current increased greatly, contrary to expectations. This was almost certainly due to a large increase in the effective cathode surface area. With $Cd^{++}$ solutions, a gauze-like dendritic deposit was produced. With $Zn^{++}$ or mixed solutions of zinc and cadmium a somewhat more dense deposit was produced. In all cases the deposit was very porous and of apparently large surface area. The increase in surface area had a much greater influence on the current density that did the stirring or agitation.

When selectively plating cadmium, at an applied potential of -0.80 volts versus $Cu/CuSO_4$, the coatings were not very adherent. Large portions of the coatings would detach or partially detach from the cathode surface. Appropriate changes in the current density were noted to coincide with these events. Some of these transients occurred instantaneously and

had extremely large absolute magnitudes. The plated solids that detached from the cathode did not immediately redissolve and appeared to have a long residence time in the solution.

When plating both cadmium and zinc, at an applied potential of -1.45 volts versus $Cu/CuSO_4$, the coatings were more adherent and uniform. The pores in the coating surface were approximately 0.03 inches in diameter. The substrate was visible through these pores. The pores were probably due to gas generated at the cathode surface during the plating process. Concentrations of less than 0.5 ppm cadmium and 15 ppm zinc were achieved in less than 24 hours.

An additional test to check the 7 liter process instrumentation using the glassware cell was performed. The cell was operated for 2-1/2 hours with currents in excess of 100 ma being noted. While a large amount of material was obviously plated, the coating was not particularly adherent. A large amount of plated material was observed circulating in the solution. The final concentrations of cadmium and zinc were 26 and 55 ppm, respectively.

While the mass balances in the above tests were greater than 95 percent, the coulombic efficiencies were relatively poor, less than 20 percent. It should also be noted that the acidity of the test solutions increased by an order of magnitude in less than 24 hours. This decrease in solution pH is due to the electrolysis of water to $O_2$ and $H^+$ that occurs at the anode. Study of the current versus plating time curves at -0.80 and -1.45 volts applied potential leads us to the conclusion that the hydrogen overvoltage has been lowered to less than -1.45 volts during the tests. This is largely due to the substantial decrease in the pH that occurs as the electrolysis proceeds.

In conclusion these tests showed that electrolysis of cadmium and zinc solutions at an initial pH of 4 produced porous dendritic deposits that were sometimes poorly adherent. Large increases in current density were produced by the increase in cathode surface area. Nearly total depletion of the dissolved metals has been demonstrated but the coulombic efficiency was very poor due to a decrease in solution pH and substantial $H_2$ evolution at the cathode.

## TABLE 4

PLATING TESTS - SUMMARY OF ANALYTICAL RESULTS

| Test ID | pH Initial | pH Final | Metal In Initial Solution | Metal In Final Solution | Metal Removed from Solution | Wt. of Solids Filtered | Metals Analyzed from Filtered Solids | Mass Balance | Total Time | Coulombs to Remove (Cd/Zn) | Total Coulombs | Coulombic Efficiency | Anodes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 4 | 2.9 | 0.1337g. | 0.0721g. | 0.0616g. | ---- | 0.0602g. | 97.7% | 22.8 hrs. | 114 | ---- | ---- | graphite |
| II | 4 | 2.9 | 0.1433 | 0.0099 | 0.1334 | 0.1810+ | 0.1380 | 96.7 | 17.7 | 308 | 2851 | 10.8% | graphite |
| III | 4 | -- | 0.1295 | 0.0567 | 0.0728+ | 0.0760+ | ---- | -- | -- | -- | --- | ---- | graphite |
| IV | 4 | 4.3 | 0.1410 | 0.0019 | 0.1391 | 0.4199* | 0.0780 | 56.1 | 28.5 | 330 | 1641 | 20.1 | Al |
| V | 4 | 2.7 | 0.1260 | 0.0503 | 0.0757 | 0.0694 | 0.0606 | 80.1 | 24.0 | 154 | 1221 | 12.6 | $PbSO_4$ |

+ includes weight of graphite filtered

* includes weight of aluminum filtered

## SECTION 6

## BENCH SCALE TESTS

### OBJECTIVES

The purpose of this project was to develop a process for the removal of toxic metals from sewage sludge. Benchscale tests were performed to demonstrate the feasibility of the electrochemical process and to confirm the usefulness of the operating conditions suggested by the laboratory scale tests. In particular it was desired to obtain a metals balance around the reactor and from it to calculate the coulombic plating efficiency as a function of test conditions.

### EXPERIMENTAL APPARATUS

Figure 14 presents a flow schematic for the demetalization test apparatus. It consists of a 7-liter rectangular plexiglas vessel equipped with nine parallel plate electrodes being alternately made of 1100 Aluminum (cathodes) and graphite (anodes). A 2.5-cm diameter copper sulfate reference electrode has been placed into solution near the electrode rack (Figure 15). Power is provided by a constant voltage (or constant current) supply via a network of switches and wires (not shown) and a Magnar model 4700M research potentiostat and its associated meters and recorders (figure 16). A gas sparger is located at the bottom of the electrolytic cell to allow oxygen, or other gas, to be bubbled into solution. A separate holding vessel (figure 17) connected to the electrolytic cell by a common channel at the vessel bottom, contains a mixer and temperature controller. A variable speed pump (figure 18) forces the fluid to recirculate from the holding vessel back to the top of the electrolytic cell where it again flows downward between the parallel plate electrodes. A plexiglas manifold was constructed to distribute the fluid evenly over the electrode channels. Critical dimensions of the test apparatus are as follows:

| | |
|---|---|
| Total sludge volume | 18.5 liters |
| Electrode chamber | 10.8 cm x 15.25 cm x 80.65 cm |
| Working volume | 52.1 cm from bottom |
| Holding chamber | 14.9 cm x 15.25 cm x 62.9 cm |

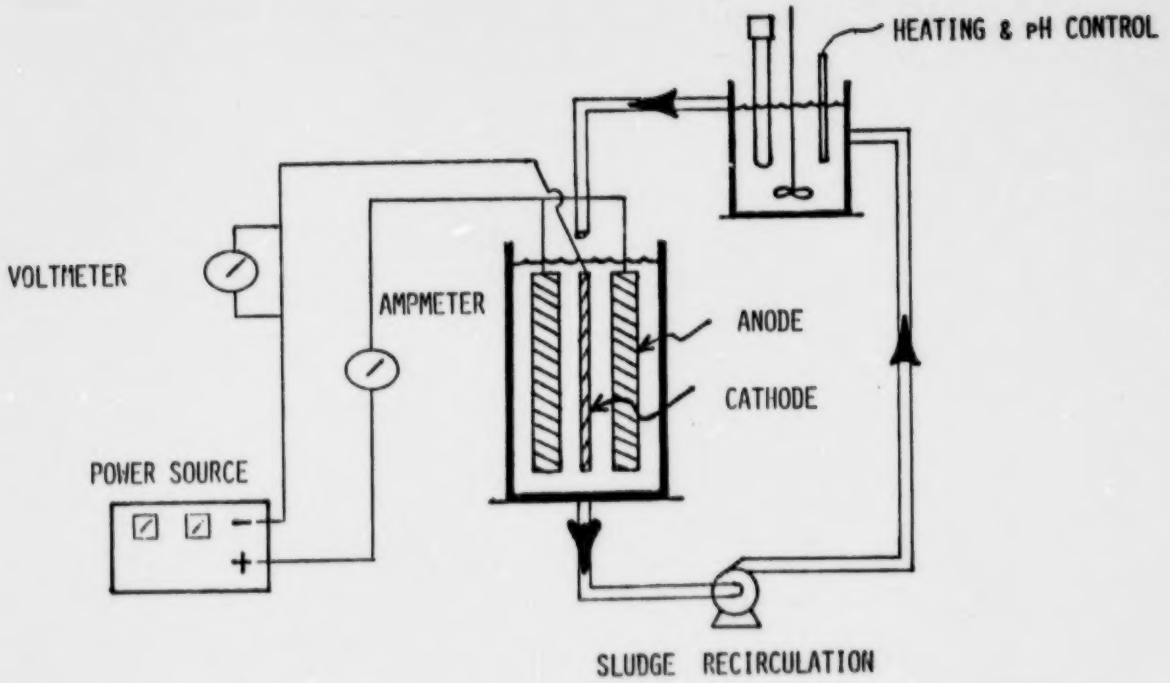



Figure 14 UC Sludge Demetallization Flow Schematic-Bench Scale Tests

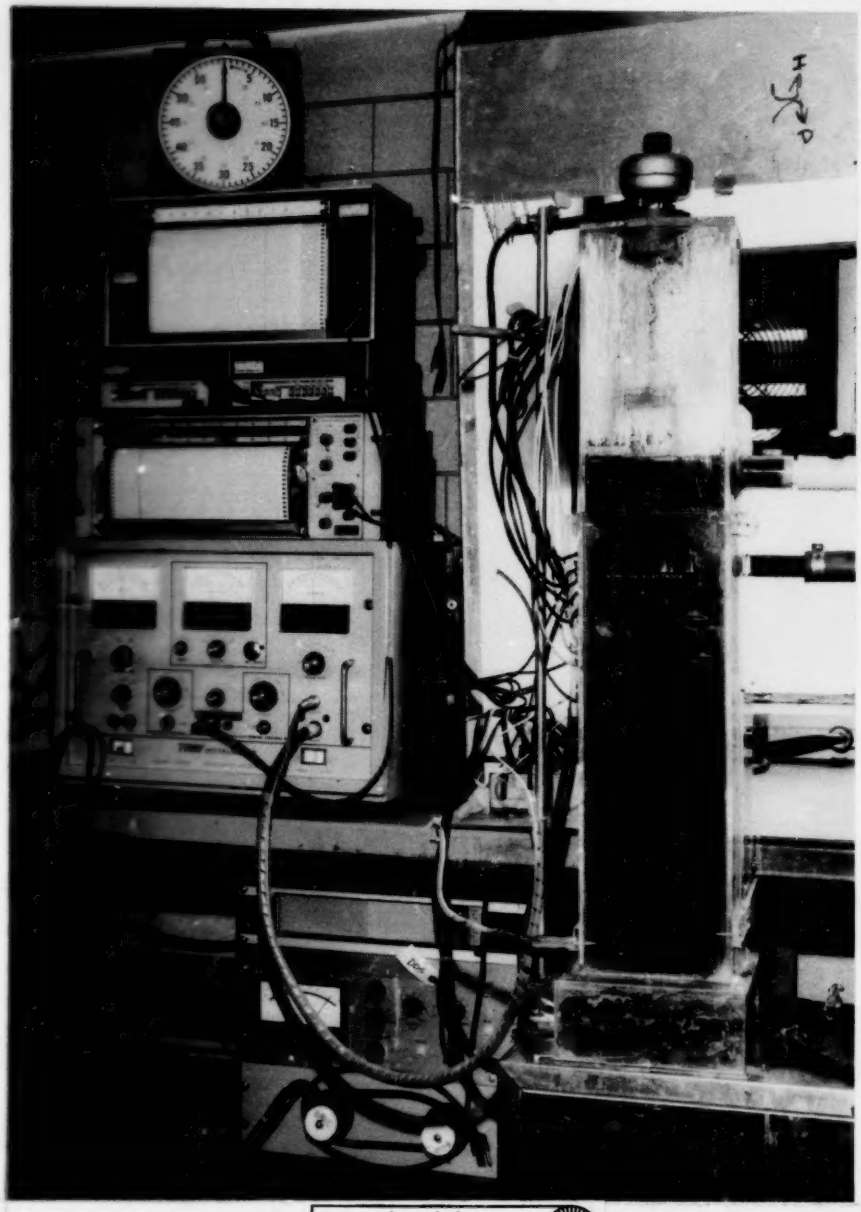


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Figure 16 Demetalization Reactor and Associated Instrumentation

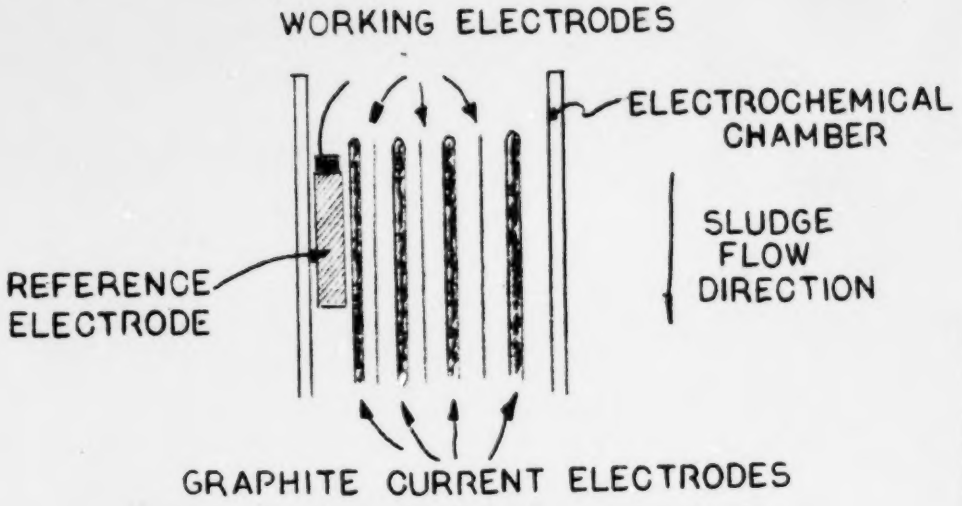


Figure 15 Bench Scale Electrode Arrangement

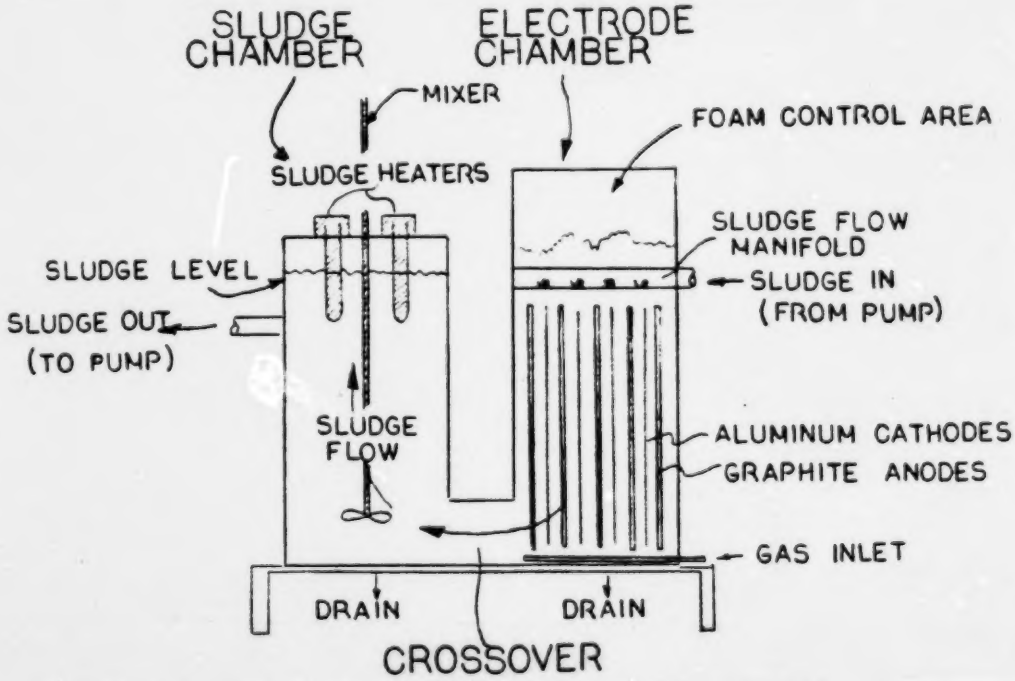


Figure 17 Bench Scale Reactor and Holding Vessel

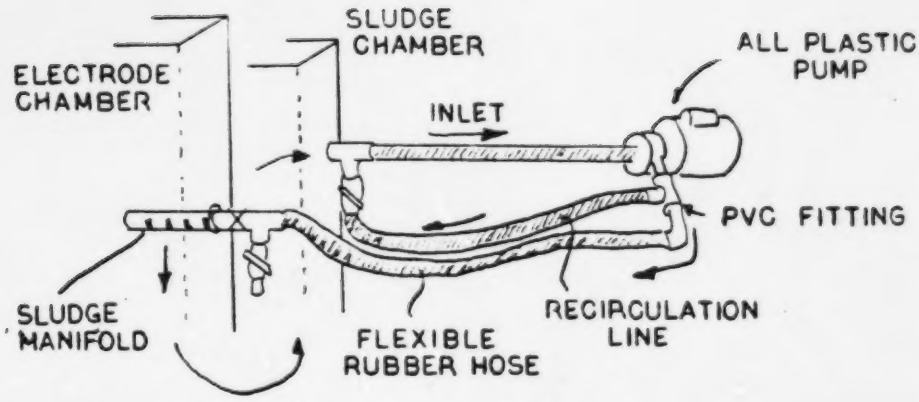


Figure 18 Bench Scale Recirculation Pump and Piping

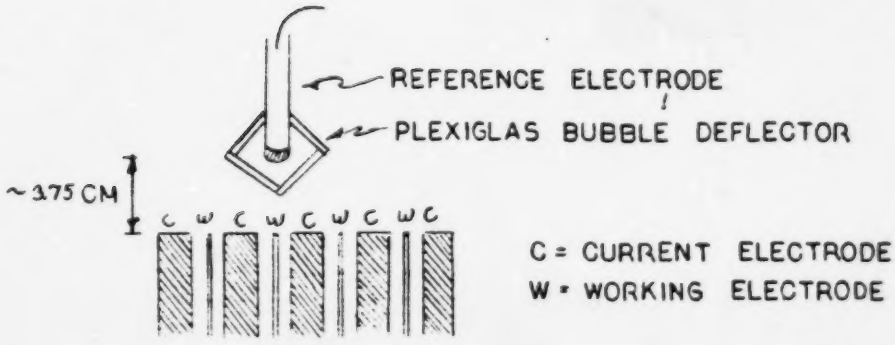


Figure 19 Plexiglas Shield for Reference Electode

| | |
|---|---|
| Working volume | 52.1 cm from bottom |
| Electrodes sit 7.6 cm from bottom up to 38.1 cm from bottom | |
| Electrode spacing | 0.95 cm |
| Manifold diameter | 1.91 cm |

After initial testing some modifications were made to the apparatus to improve performance. The nature of these improvements are as follows:

1) A small plexiglas shield (figure 19) was constructed around the tip of the reference electrode to prevent interference by rising gas bubbles.

2) Metal components (such as screws, gauges, etc.) in the apparatus structure were identified as a source of metal contamination and were removed.

3) The stainless steel rotor of the recirculation pump was replaced by equivalent drive coated with GE Glyptol 1201-A insulating enamel to prevent corrosion.

4) Alligator clips which had been used to make anode connections were found to be a source of cadmium contamination in early tests (figure 20). These clips were replaced by insulated copper wire adhesive bonded into a hole drilled into the carbon anode. A silicone rubber cement was used to seal the connection from the electrolyte (Figure 21).

5) Additional gas space volume was added to the electrolytic reactor to prevent foam overflow. Due to a desire to operate without chemical anti-foam addition, the apparatus was provided with a rotating paddle above the liquid level which beat down any foaming which did occur.

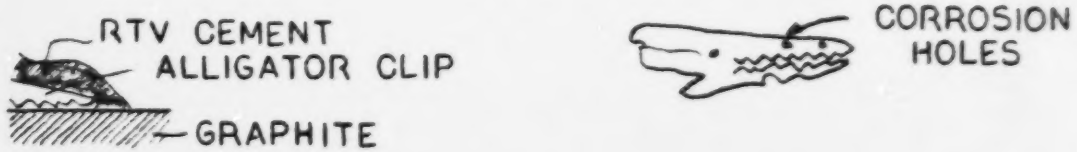


Figure 20 Sketch of Alligator Clip Corrosion

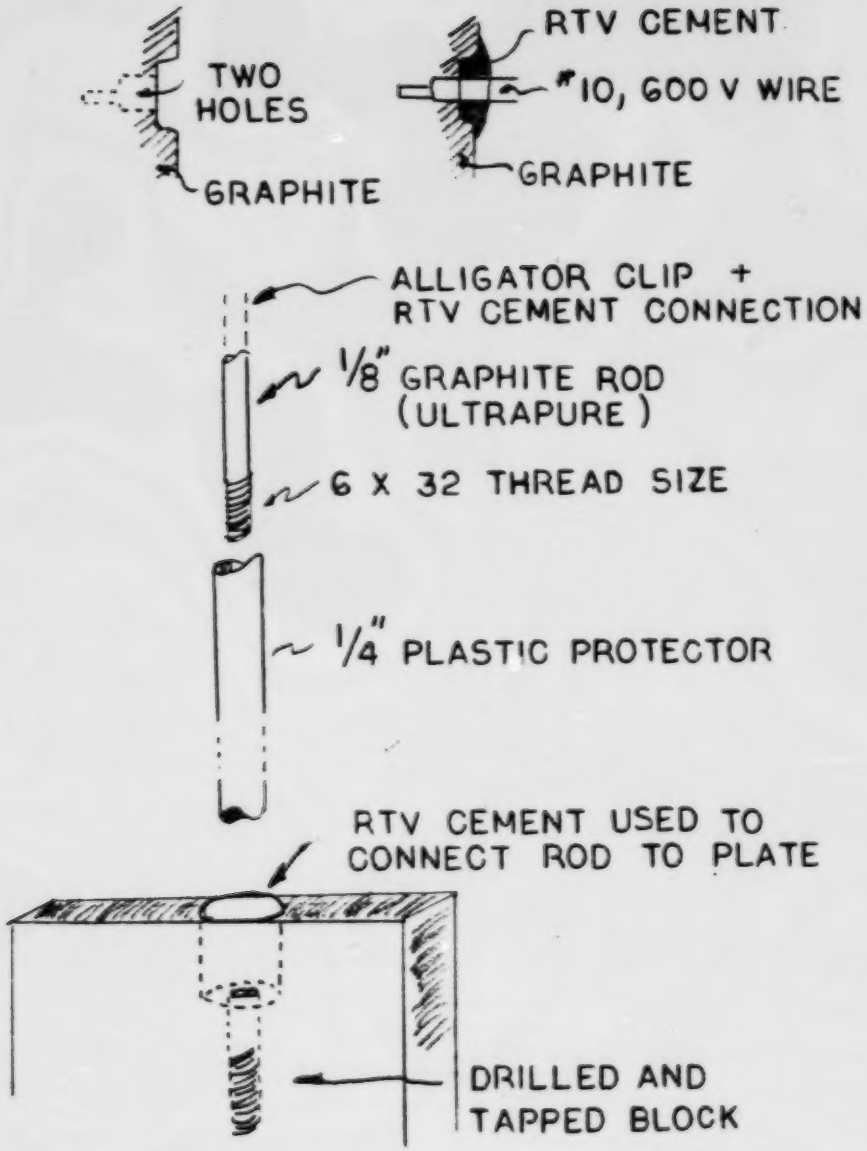


Figure 21 Sketch of Modified Anode Connection

PROCEDURES

Prior to the start of testing the amount of recirculation flow as a function of pump rpm was determined via the valve apparatus illustrated in figure 18. Furthermore the effectiveness of sludge distribution from the manifold was calibrated by collecting and measuring the liquid volume from each slot at minimum, maximum and intermediate flowrates. Each anode and cathode was labeled for identification, cleaned with soap solution and rinsed with distilled water.

Secondary sludge was obtained from the Lockport, New York, Wastewater Treatment Plant on a weekly basis and kept in refrigerated storage. When ready for use the sludge was gravity thickened and fed to two 14 liter Microferm fermenters equipped with variable speed mixers, a gas sparger and heating coil (figures 22-23). In these reactors the sludge was aerobically digested at 50-55°C for a period of ~ 1 day. The sludge was then screened through a 3/16-inch mesh and fed to the demetalization reactor. The recirculation pump, mixers and sludge heaters were adjusted to their desired set points and turned on. The pH of the sludge was adjusted by the addition of 10N $H_2SO_4$. Gas purge from a regulated cylinder provided agitation between the electrodes.

After approximately 5 minutes of operation to allow for homogeneity to develop throughout the system, a sludge sample was withdrawn as the initial sample. The electrical current was then applied and the total cell voltage adjusted to maintain the desired reference voltage. Readings and samples were then taken at intervals during the course of each test. Total cell voltage, reference voltage and total cell amperage were recorded continuously while the following data were hand recorded:

time
gas flowrate
sludge recirculation flowrate
temperature
pH
reactor volume
amount of acid addition (if any)

The volume of each sludge sample withdrawn was recorded and at the conclusion of each test the reactor was emptied, its contents measured and any water loss due to evaporation made up by addition of distilled water. The electrodes were removed, any observations as to the condition of the metal deposits noted, and then each was sent to the laboratory in a separate beaker for analysis.

Procedure for Heavy Metals Analysis of Test Samples and Electrodes

1) All glassware used were cleaned with nitric acid and rinsed thoroughly with deionized water.

2) All metals were analyzed on a Perkin-Elmer 460 Atomic Absorption spectrophotometer, with flame technique.

3) All stock standard solutions were purchased from Fisher Scientific Company. Diluted Standards are made in 5% nitric acid.

4) Sample solutions were prepared as follows:

a) Sludge: A measured volume (100-150 ml) of sludge was transferred into a 600 ml beaker and 10 ml of nitric acid added. The mixture was then evaporated until dry. Another 5 ml of nitric acid along with 50 ml of water was then added and the mixture boiled gently fo 5-10 minutes. The sample was then transferred to a 100 ml volumetric flask, made up to volume, mixed and then allowed to settle. The clear supernatant which results was used for metal determination. Dilution is necessary for all elements except cadmium.

b) Electrode deposits: The deposit was removed by rinsing the surfaces with a 100 ml solution containing 20 ml nitric acid. The rinsing was repeated with the aid of an eye dropper until the electrodes were clean. The rinse solution was combined with any drippings in the sample beaker and made up to 250 ml. Dilution was necessary for all elements.

Total and volatile solids content of the sludge samples were determined by the procedures outlined in Standard Methods for the Examination of Water and Wastewater.

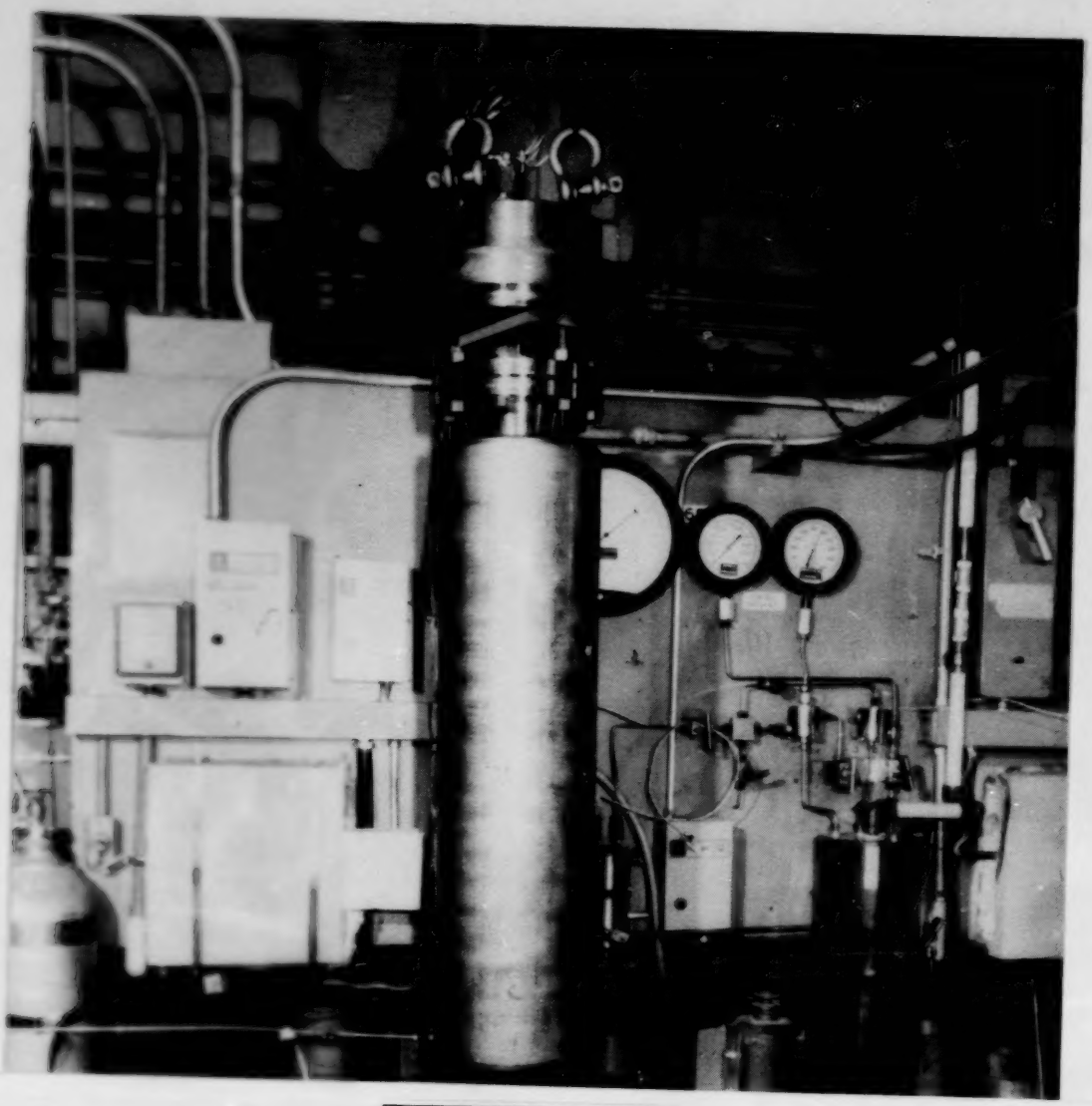

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Figure 22 Fermenter Vessel

Figure 23 14 Liter Microferm Fermenter System

## RESULTS

### Sludge Tests

The bench scale demetalization reactor was modified as described in the apparatus section and preliminary tests run to check out system performance, experimental operating techniques and sample analysis procedures. These runs used secondary sludge from the Lockport N.Y. Waste Treatment Plant which had varying concentrations of metal ion species. Table 5 presents the "as received" sludge metal composition.

Upon completion of these initial tests several important observations immediately came to light. First it was observed that the total cell voltage was 1 to 2 volts lower than that normally used in previous tests despite reference potentials (vs the Cu-$CuSO_4$ electrode) in the -1.0 to -1.5 volt range. This suggested that much of the power input of previous tests may have been wasted on unwanted side reactions. The second important conclusion was that the most electronegative metal, zinc, could indeed be plated out at these low cell voltages. Thirdly, it was found that the amount of material plated (as determined by removing and analyzing electrode deposits) was substantially more for certain metal ions species that the amount of metal removal (as determined by a metals balance) based on solution concentrations. This discovery led to an extensive search for possible contamination sources in the bench scale apparatus.

The bulk of the remaining sludge tests were oriented towards eliminating various sources of contamination such as reactor screws, fittings, recirculation pump and electrode clips. That this program was fairly successful is shown in Table 6 by a change in the metal balances from negative to positive indicating contamination free operation. Unfortunately the coulombic efficiency as defined as (coulombs metals plated/coulombs input to electrodes) x 100 were all extremely low with the highest being less than 10%. Furthermore, the percentage of metals removed from solution were also disappointingly low. In tests 8 to 17 where positive metal balances were achieved the removal rate averaged 26.5% for Zinc, 57.2% for Cadmium, 21.9% for Nickel and 83.2% for Copper. Details of these tests as well as sketches and descriptions of electrode surface deposits can be found in appendix D.

TABLE 5

Metals Concentration
(mg/kg total mass)

Lockport, New York Sludge

| Date | % TS | Cu | Zn | Pb | Ni | Cd | Cr |
|---|---|---|---|---|---|---|---|
| 11-04-80 | 2.61 | 52 | 164 | 64 | 12 | 0.89 | 23 |
| 11-13-80 | 2.06 | 51 | 119 | 57 | 9.7 | 0.75 | 26 |
| 11-19-80 | 1.48 | 35 | 57 | 33 | 5.9 | 0.63 | 14 |
| 11-21-80 | 1.63 | 36 | 58 | 35 | 6.8 | 0.67 | 16 |
| 12-17-80 | 1.96 | 36 | 65 | 30 | 8.5 | 0.50 | 18 |
| 01-06-81 | 1.14 | 20 | 33 | 15 | 3.0 | 0.46 | 14 |
| 01-12-81 | 1.83 | 25 | 41 | 22 | 6.2 | 0.24 | 15 |

## Metal Ion Solution Tests

After the eighth demetalization test the electrolyte was changed to a synthetic solution of cadmium, copper, zinc and nickel ions in distilled water. The purpose of this change was to allow a more accurate determination of a reactor metal balance and to provide visual monitoring of the electrodes during testing. Despite the elimination of any possible interference due to the sludge solids, the metal removals and plating efficiencies still remained low. This observation suggests that a short coming of the electrochemical process itself may prevent the attainment of better performance rather than any characteristics of the sludge.

Results obtained from the laboratory scale apparatus during this time allowed hope for improved metal removal. It was observed in these small scale tests that a porous, dendritic structure of plated metals formed on the cathode the composition and structure of which was dependent on the electrode materials used. During the course of a test some pieces of the metal deposit were found to spall off the cathode due to agitation of the bath. This spalled material remained suspended in the bath solution as particles or chips of metal and were uncounted as plated metal. Furthermore these particles act as points of high metal concentration in the solution making it non-homogeneous and increasing the difficultly of withdrawing representative liquid samples for analysis. This problem was addressed in Tests 14 to 17. In these tests sampling procedures were modified to account for the plated material which spalls off the electrodes and back into bulk solution. This was done by filtering each sample, the final reactor fluid, and each reactor wash to collect any particulate matter. The liquid and electrodes samples were then analyzed in the usual way and the filtered solids analyzed for their metals content. Such procedures did improve metal balances in the 17 liter reactor to within 25% which may be a reasonable limit given the accuracy of the large scale analysis.

TABLE 6

17 LITER DEMETALIZATION TEST SUMMARY

| TEST NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DATE | 11-4 | 11-12 | 11-19 | 11-21 | 12-17 | 1-6 | 1-12 | 1-20 | 1-26 | 1-29 | 2-2 | 2-9 | 2-24 | 3-9 | 4-9 | 4-23 |
| TEST LENGTH, HRS. | 5 | 23 | 5 | 6 | 23 | 24 | 23 | 23 | 24 | 24 | 24 | 23 | 22 | 23 | 19 | 21 |
| FLUID | LS | LS | LS | LS | LS | LS | LS | LS | SS | SS | SS | SS | SS | SS | SS | LS-S |
| TEMPERATURE, °C | 55 | 52 | 54 | 48 | 49 | 50 | 47 | 48 | 40 | 46 | 45 | 49 | 50 | 47 | 43 | 38 |
| pH | 4.0 | 3.9 | 4.0 | 4.2 | 4.2 | 3.6 | 3.8 | 4.3 | 3.8 | 3.8 | 2.9 | 2.6 | 2.3 | 3.0 | 3.8 | 6.0 |
| AEROBIC PRETREATMENT HRS. | 24 | 24 | 23 | 24 | 23 | 24 | 21 | 24 | - | - | - | - | - | - | - | - |
| REFERENCE VOLTAGE | 1.20 | 1.50 | 1.06 | 0.96 | 1.50 | 1.50 | 2.00 | 1.30 | 1.30 | 1.40 | - | - | 1.40 | 1.46 | 1.40 | 1.40 |
| TOTAL CELL VOLTAGE | 2.02 | 2.79 | 1.06 | 1.85 | 2.64 | 2.85 | 2.92 | 2.61 | 2.40 | 2.60 | 3.08 | 3.14 | - | 1.40 | 3.00 | 2.50 |
| TOTAL AMPERAGE | 0.654 | 0.863 | 1.390 | 0.494 | 0.614 | 1.649 | 3.660 | 0.650 | 0.340 | 0.690 | 1.558 | 1.333 | 1.72 | 0.942 | 0.078 | 2.06 |
| GAS FLOW (SCFH) | 5(AIR) | 5(AIR) | 5(AIR) | 5(AIR) | 4(AIR) | 4(AIR) | 4(AIR) | 4(AIR) | 4(N2) | 4(N2) | 4(N2) | 4(N2) | 4(N2) | 4(N2) | 4(N2) | 4(N2) |
| FLUID FLOW (l/min) | 16 | 16.4 | 16.7 | 16.9 | 27.0 | 50.0 | 26.0 | 26.0 | 49.5 | 27.0 | 18.6 | 18.1 | 17.3 | 19.4 | 21.3 | 19.3 |
| % METAL REMOVAL ((INITIAL-FINAL/INITIAL) x 100) | | | | | | | | | | | | | | | | |
| Zn | 14.3 | 6.4 | 0 | 0 | 4.1 | 35.0 | 31.2 | 48.9 | - | 80.6 | 6.5 | 14.3 | - | 20.2 | 4.6 | 10.2 |
| Cr | 0 | 0 | 0 | 0 | 0 | 9.4 | 15.8 | 21.4 | - | - | - | - | - | - | - | - |
| Cd | 0 | 54.5 | 52.7 | 0 | 0 | 25.7 | 0 | 65.3 | - | 21.7 | 72.1 | 69.5 | - | 99.5 | 37.5 | 34.9 |
| Ni | 8.2 | 0 | 0 | 0 | 11.9 | 50.0 | 73.4 | 45.3 | - | - | 10.3 | 10.0 | - | - | - | - |
| Pb | 18.7 | 0 | 0 | 4.7 | 0 | 28.4 | 7.3 | 12.7 | - | - | - | - | - | - | - | - |
| Cu | 9.2 | 25.2 | 39.5 | 34.5 | 2.4 | 82.4 | 37.8 | 73.6 | - | - | 85.1 | 91.0 | - | - | - | - |
| % METAL BALANCE ERROR ((REMOVED - PLATED)/REMOVED) x 100 | | | | | | | | | | | | | | | | |
| Zn | | | | | | -42.4 | -29.6 | 88.6 | - | 99.7 | 99.2 | 99.7 | - | 26.4 | 96.2 | -10.8 |
| Cr (Negative indicates more | | | | | | -38.0 | -91.7 | 93.9 | - | - | - | - | - | - | - | - |
| Cd metals plated than removed) | | | | | | -123.0 | 0 | 4.2 | - | -118.0 | 56.2 | 10.6 | - | 33.8 | 13.6 | -15.8 |
| Ni | | | | | | -14.1 | -44.2 | 7.5 | - | - | 99.9 | 92.3 | - | - | - | - |
| Pb | | | | | | 30.7 | -81.3 | 49.5 | - | - | - | - | - | - | - | - |
| Cu | | | | | | -11.5 | 7.3 | -38.9 | - | - | 68.9 | 42.7 | - | - | - | - |
| % COULOMIC EFFICENCY PLATED | 0.9 | 8.1 | 1.2 | 9.3 | 1.8 | 2.2 | 0.4 | 4.9 | - | 3.5 | 1.7 | 4.4 | 1.4 | 2.4 | 1.8 | 0.06 |

LS = Lockport Sludge
SS = Synthetic Fluid
LS-S = Lockport Sludge Supernatant

The difficulties in obtaining a reliable metals balance in the 17 liter reactor points out the need to eliminate stray currents and rogue metal sources in equipment design. However the tests do demonstrate that controlled potential electrodeposition of metals from wastewater sludge is a viable process although the low coulombic efficiencies experienced may prevent it from being an economical one. Furthermore the metals seem to form a rather lightly bound deposit on the cathode, the bulk of which is fairly easily removed by scraping or brushing. Unfortunately some of this deposited material is so poorly adherent that is spalls off the cathode during normal agitation. Filtration or settling of the sludge to remove this spalled material does not seem a practical alternative. Further data and observations regarding the 17 liter tests can be found in Appendix D.

# APPENDIX A

## DROPPING MERCURY TESTS

### Tests 1 - 2

In neither case is the current (y) axis calibrated but by comparison one can see the effect which the presence of oxygen in the aeration gas has on the shape of the polarogram. The oxygen interference takes the form of a current rise at approximately -0.3 volts and a sharp "glitsch" in the curve at -0.78 volts. Deaerating with nitrogen prior to testing removes these phenomena.

### Tests 3 - 4

This pair of tests were intended to show the effect which the addition of suppressant has on the shape of the polarogram. Suppressant takes the form of organic materials such as Agar, gelatin or methyl-red which act similar to sludge solids in terms of dampening out current fluctuations. Suppressants also remove or smooth out the current "maxima" shown in the unsuppressed Zn plot. They do not seem to significantly alter the half-wave potential of zinc which is determined as approximately -1.47 volts from test (3).

These solutions were both deaerated for twenty minutes with tank nitrogen before the test run. The solution pH was adjusted to 4 with dilute $H_2SO_4$ and no supporting electrolyte was added. The analog current output of the potentiostat was conditioned with an RC filter network TC = 1 second (1 meg$\Omega$/1$\mu$f). The runs were made in the potentiostat range of 0.00 to 2.90 volts. The current (y axis) was calibrated using a 1000 resistor and the Aardvark potentiostat. These conditions will remain the same in all following tests except where noted.

A small wave in the 0-0.1 volt range in test (4) is believed to result from mercury contamination from the dropping mercury electrode. When fresh solution is tested this wave disappears.

Tests 5 - 6

The result of adding even a small amount of silicone based antifoam agent to the solution is a perceptible shift of the zinc half-wave or "knee" to a more cathodic value (more to the right). Note the maxima is still evident since no suppressant was added.

Tests 7 - 8

These blanks were prepared to study the effects which various additives have on the dropping mercury apparatus. Except for the leading edge of $H_2$ evolution wave at approximately -1.6 volts there seems to be no effect.

The 0.2% gelatin solution was prepared by boiling deionized water, allowing it to cool to 60°C and dissolving 0.2 grams gelatin (UPS) per 100 ml water. A single crystal of phenol or thynol was then added.

Tests 9 - 10

Chromium solution polarograms for suppressed and unsuppressed cases are illustrated. The half-wave potential seems to be approximately -1.35 volts.

Tests 11 - 12

The comparison of these two plots illustrates the iron reduction wave just superimposed on the $H_2$ evolution wave at approximately -1.8 volts.

Tests 13 - 14

Cadmium solution polarograms for suppressed and unsuppressed cases are illustrated. The half-wave potential seems to shift slightly from -0.95 volts to -0.97 volts. The cause of the slight peak at -0.4 volts is unknown.

Tests 15 - 16

Nickel solution polarograms for suppressed and unsuppressed cases are illustrated. The half-wave potential is shifted slightly from -1.53 volts to -1.40 volts.

Tests 17 - 18

The first plot illustrates the copper polarogram. Since the $E_0$ for the $Cu^{+2} + 2e$ half reaction is positive, it would be expected to plate out early at a potential close to 0.0 volts. In fact the wave seems to start at -0.2 volts and increase to -1.1 volts where a change in the current (y axis) was effected. Although this gives a half-wave potential of -0.71 volts the true value is expected to be more positive. Note the leading edge of the $H_2$ evolution curve at -2.0 volts.

The second polarogram shows a solution containing all threes ions (Cu, Cd, Zn) plus the gelatin suppressant. The following half-waves can be determined:

| | Volts | |
|---|---|---|
| Cu | -0.05 | Note that the Cd and Cu values have shifted |
| Cd | -0.85 | from the single ion runs. |
| Zn | -1.48 | |

Tests 19 - 20

The following half-wave potentials can be determined from these plots:

| | Dropping Hg ($HgSO_4$) | Copper ($Cu/CuSO_4$) | SCE ($Hg_2CL_2$) |
|---|---|---|---|
| Cu | -0.05 | -0.05 | 0.0 volts |
| Cd | -0.85 | -0.64 | -0.55 |
| Zn | -1.48 | -1.09 | -1.00 |

Tests 21 - 22

A. Agar
B. Agar plus methyl-red
C. Agar plus methyl-red plus gelatin

The polarogram of figure 21 again emphasizes that the presence of oxygen in the electrolyte disrupts the shape of the polarogram at low voltages even when other reference electrodes are utilized.

Figure 22 shows the effect of various organic suppressants on a three ion solution. The current axis was adjusted for plot C to improve visibility. Except for a minor difference (possibly due to Hg contamination) at the beginning of the plots, their shapes generally agree with one another.

Tests 23 - 24

These polarograms demonstrated the addition of a fourth metal ion, nickel, to the solution previously tested. The Ni wave seems to fall very close to the zinc wave as might be expected from their single ion potentials. The result is a single large wave so that separate half-wave potentials one difficult to define:

| | Unsuppressed | Suppressed |
|---|---|---|
| Cu | -0.10 | -0.22 |
| Cd | -0.70 | -0.90 |
| Ni | -1.43 | -1.45 |
| Zn | -1.53 | -1.73 |

The suppressant seems to shift the Cd and Zn potentials.

Tests 25 - 31

The purpose of runs was to investigate what effect, if any, concentration plays in the half-wave potential of Cd and Zn. Values are compared for several reference electrodes.

| | $CU/CuSO_4$ 10 ppm | $Hg_2CL_2$ 10 ppm | $Hg\ SO_4$ 10 ppm |
|---|---|---|---|
| Cd | -0.62 | -0.56 | -0.87 |
| Zn | -1.07 | -1.00 | -1.38 |

| | $CU/CuSO_4$ 100 ppm | $Hg_2CL_2$ 100 ppm | $Hg\ SO_4$ 100 ppm |
|---|---|---|---|
| Cd | -0.65 | -0.56 | -0.91 |
| Zn | -1.17 | -1.00 | -1.51 |

The resultant half-wave potentials seem fairly close (with the exception of the zinc in the $HgSO_4$ case) with perhaps the higher concentration being slightly more cathodic. The progression between the various reference electrodes is the same as demonstrated in previous tests.

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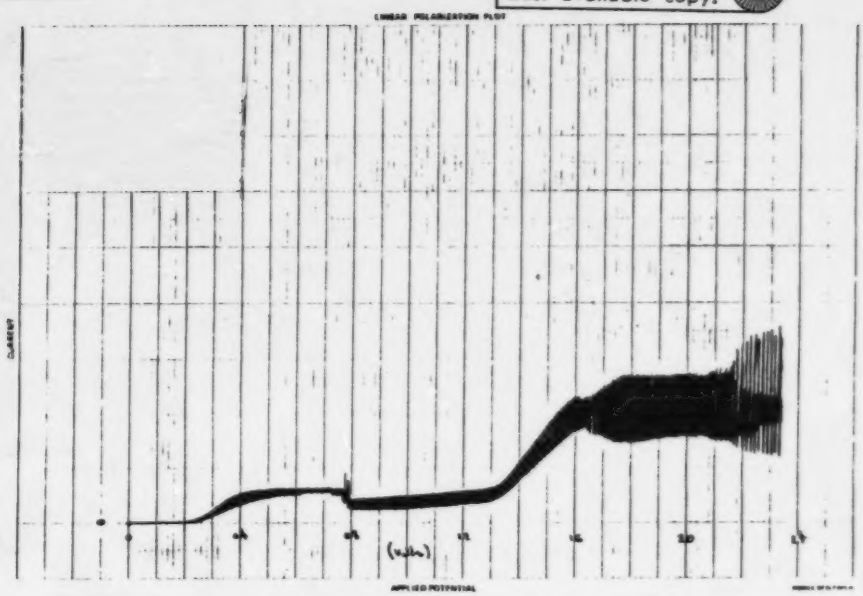

Figure A - (1): 0.0153 M Zn solution aerated before testing.

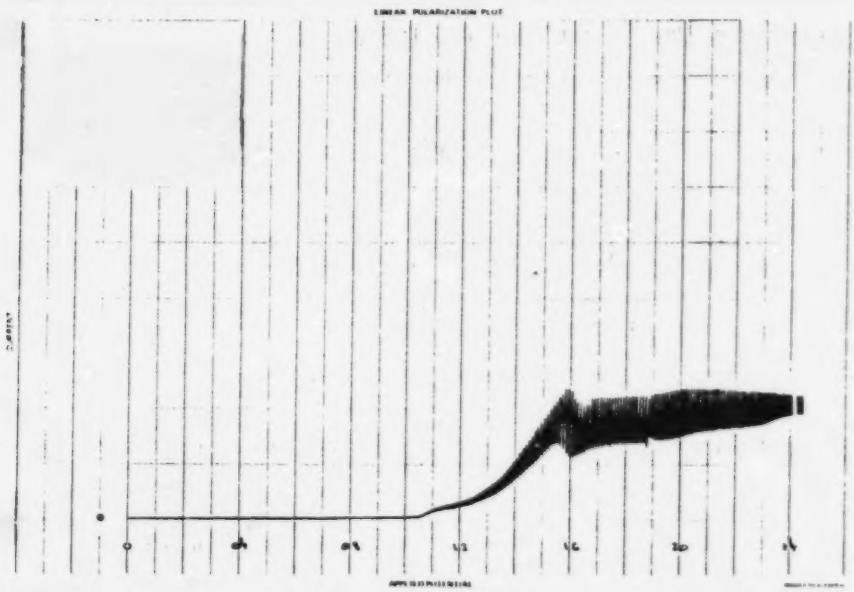

Figure A - (2): Same solution as (1) but deaeration with cylinder nitrogen for 20 minutes before testing.

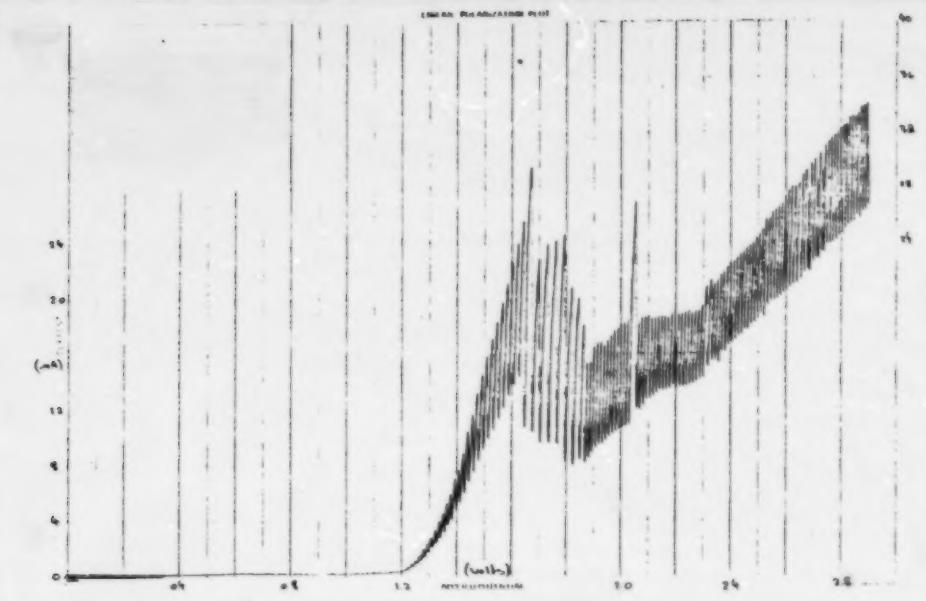

Figure A - (3): 0.0153 M Zn solution, deaerated, unsuppressed

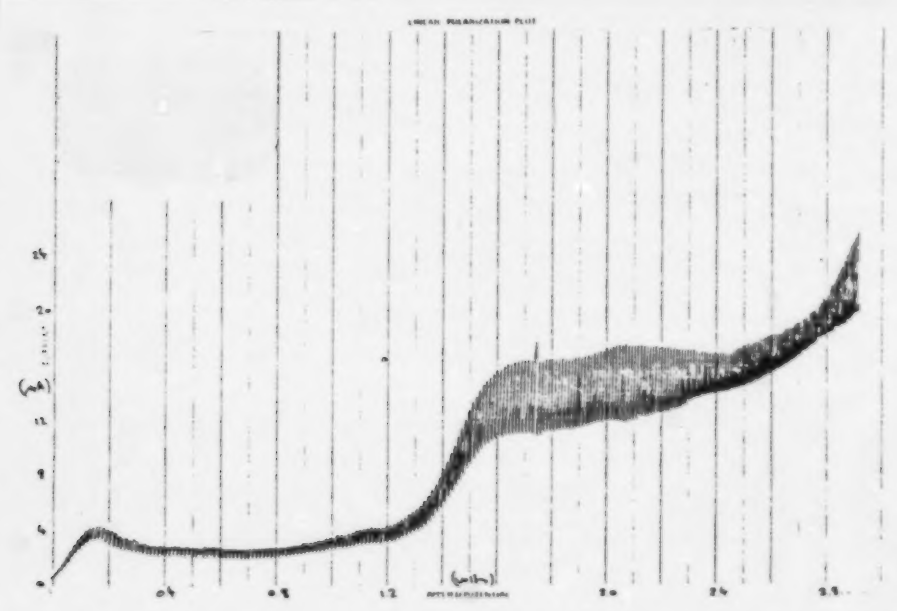

Figure A - (4): Same solution as (3) except with the addition of 0.7 ml of 0.2% gelatin solution as suppressant.

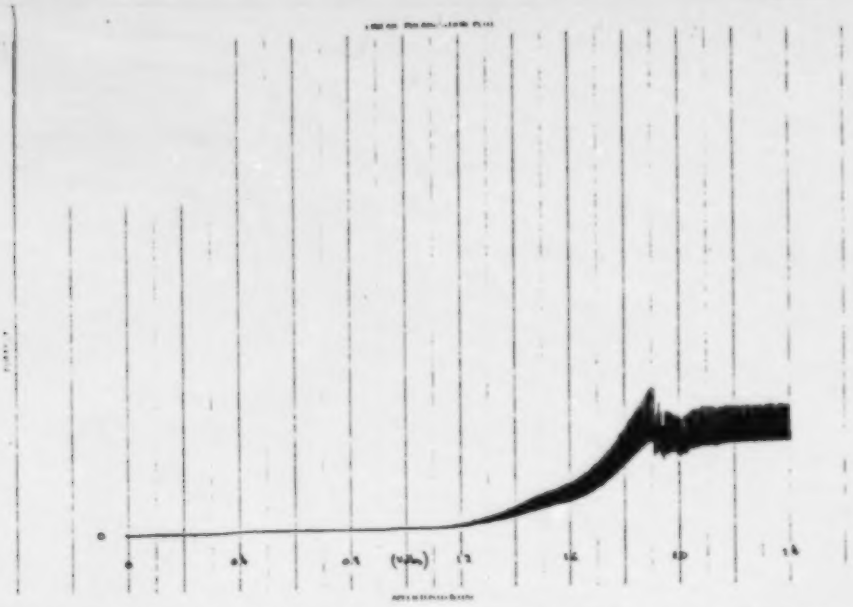

Figure A - (5): 0.0153 M Zn solution, deaerated, plus 1 drop antifoam agent

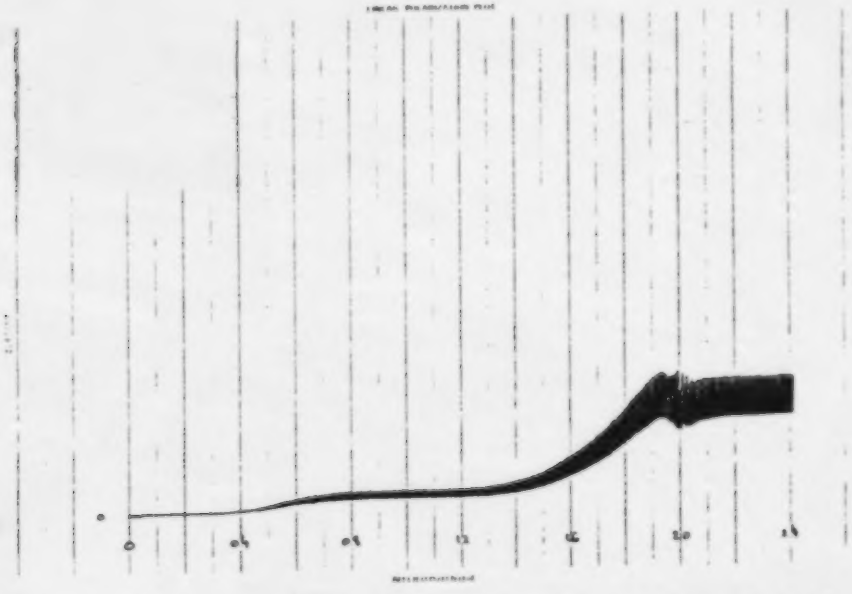

Figure A - (6): 0.0153 M Zn solution, aerated, plus 1 drop antifoam agent.

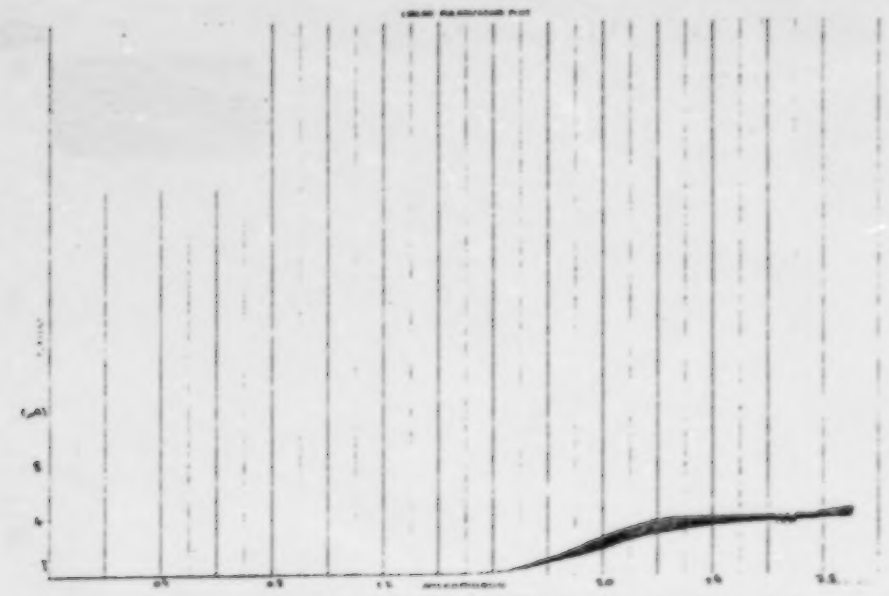

Figure A - (7): $SO_4$ blank prepared by adding $H_2SO_4$ to deionized water.

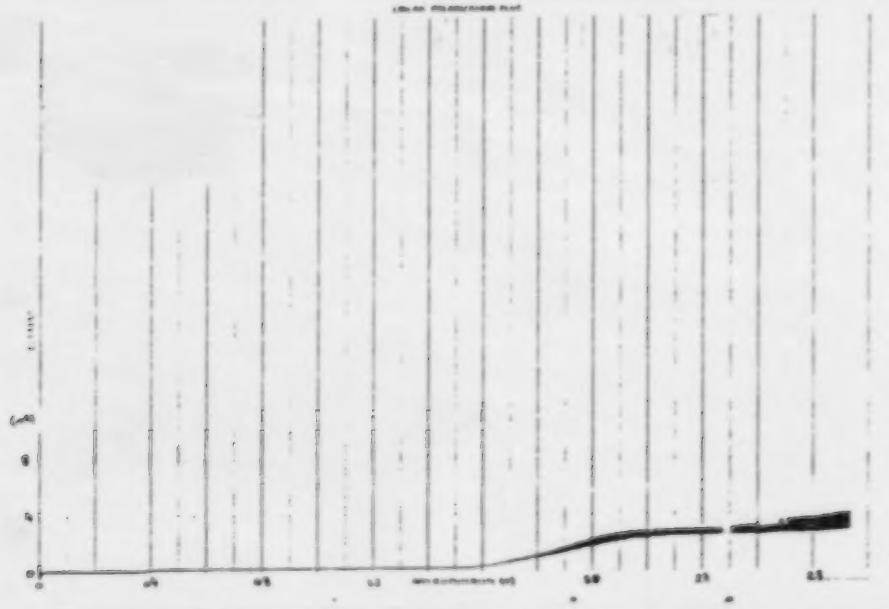

Figure A - (8): Same as (7) but with 0.7 ml of 0.2% gelatin added.

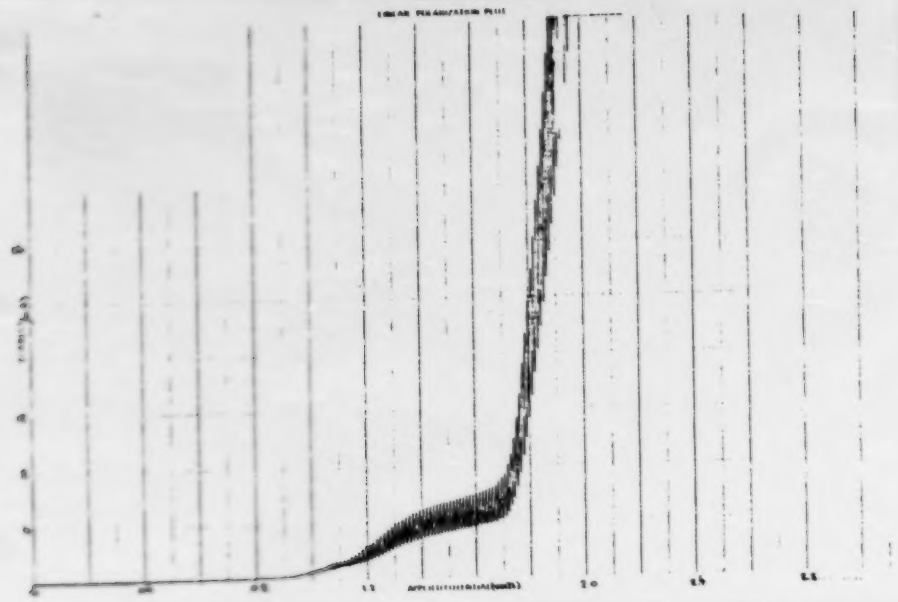

Figure A - (9): 0.0018 M Cr solution, unsuppressed.

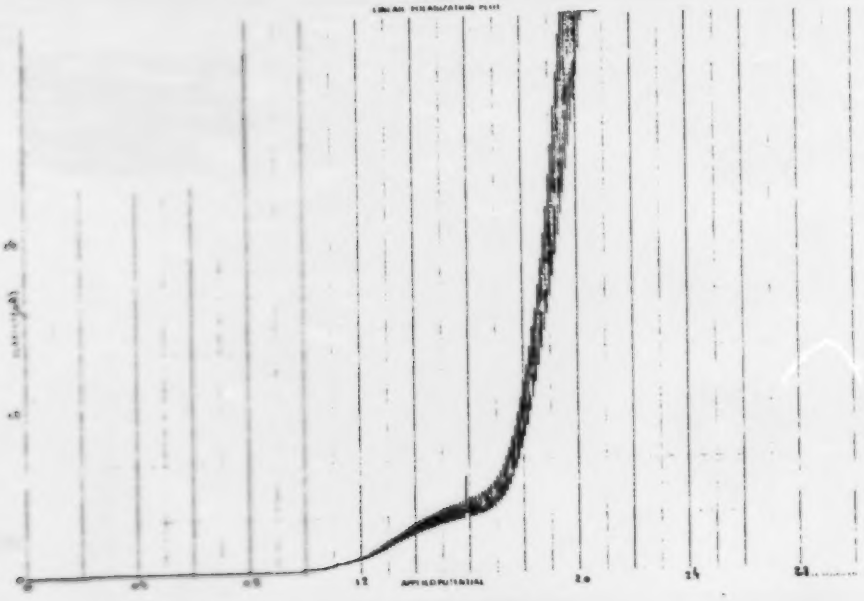

Figure A - (10): 0.0018 M Cr solution, suppressed.

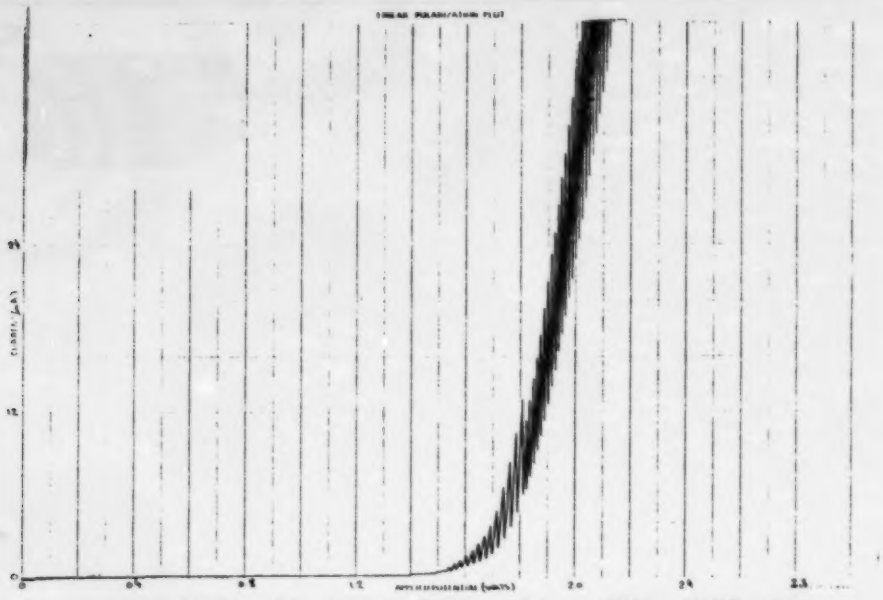

Figure A - (11): $SO_4$ blank prepared by adding $H_2SO_4$ to deionized water.

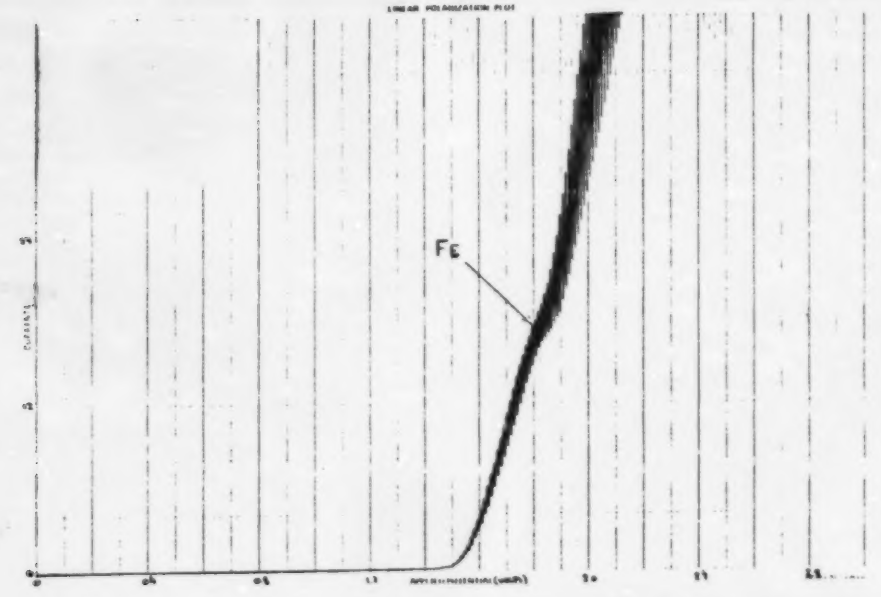


Figure A - (12): 0.00179 M Fe solution, suppressed.

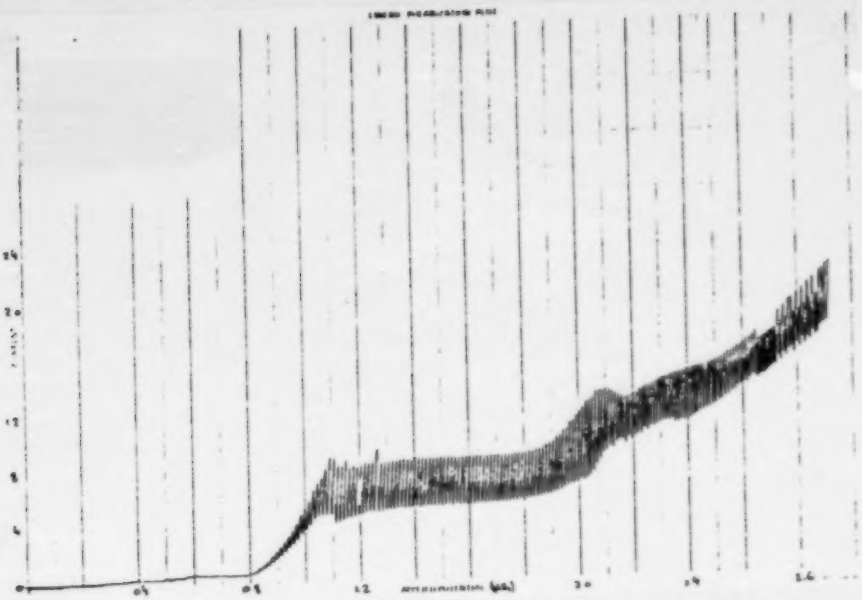

Figure A - (13): 0.00089 M Cd solution, unsuppressed.

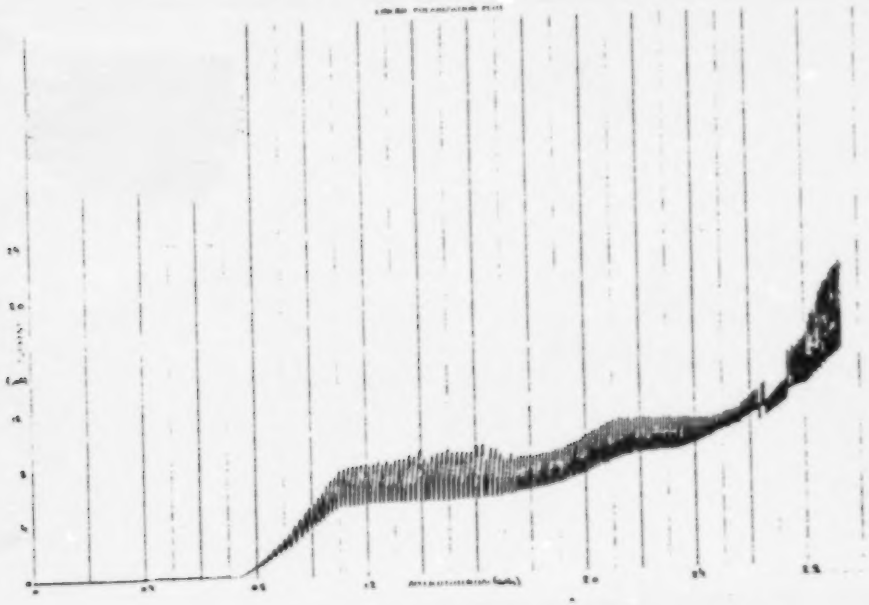

Figure A - (14): 0.00089 M Cd solution, suppressed.

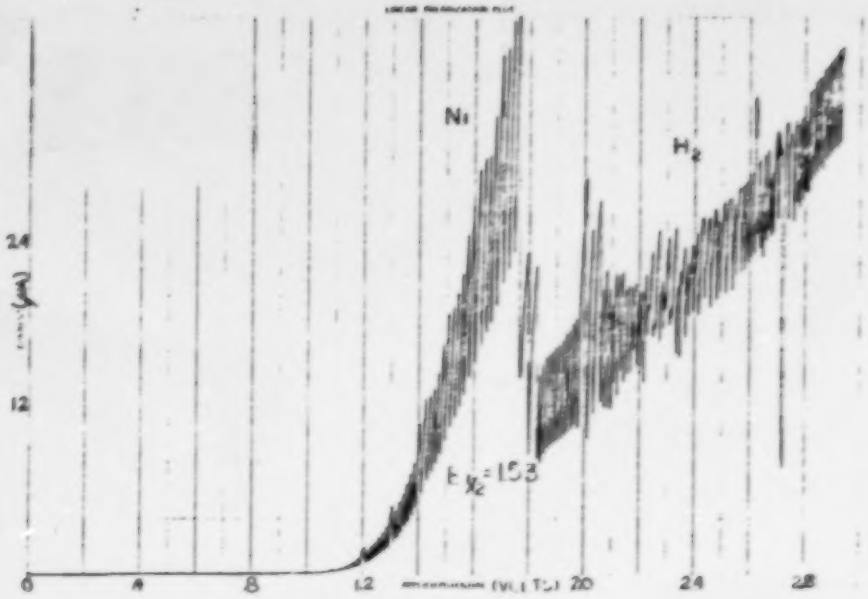


Figure A - (15): 0.0017 M Ni solution, unsuppressed.

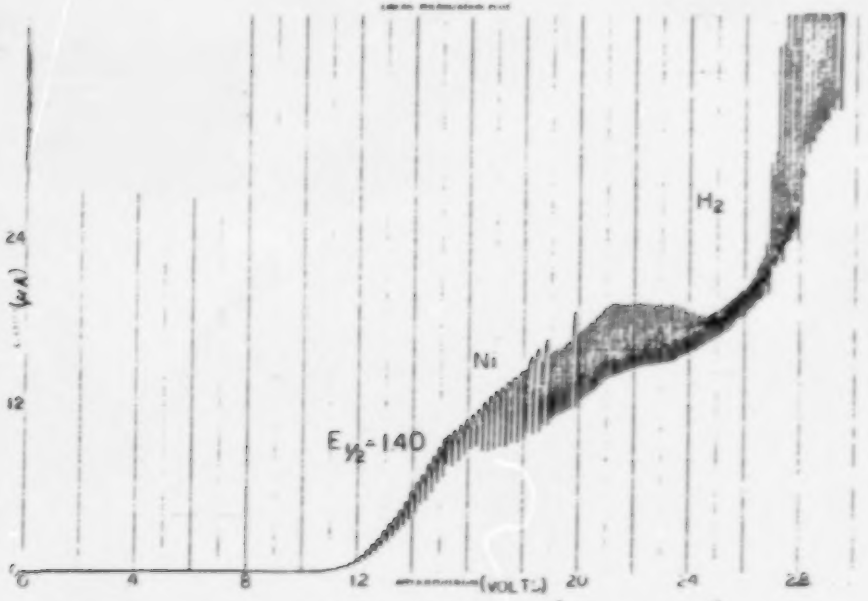


Figure A - (16): 0.0017 M Ni solution, suppressed.

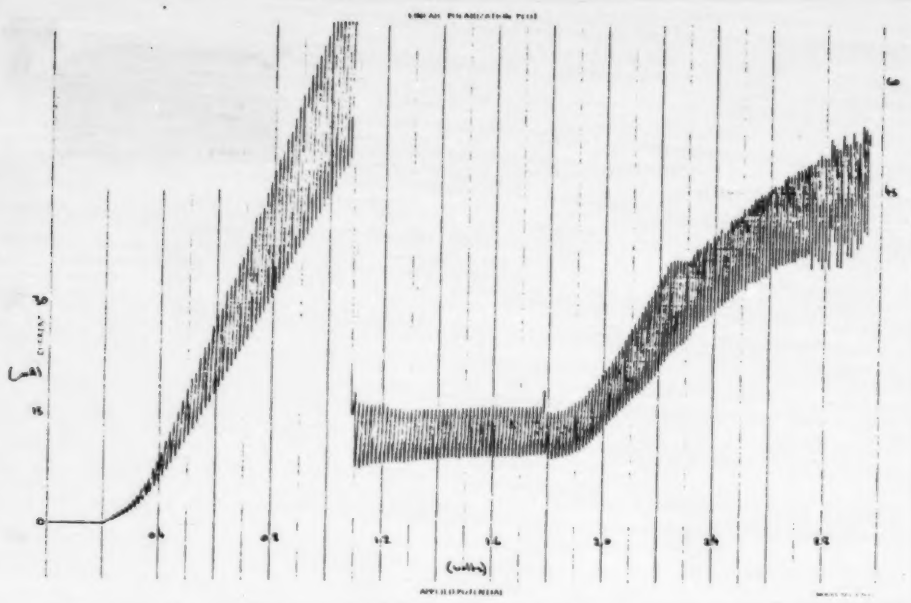

Figure A - (17): 0.00157 M Cu solution, unsuppressed.

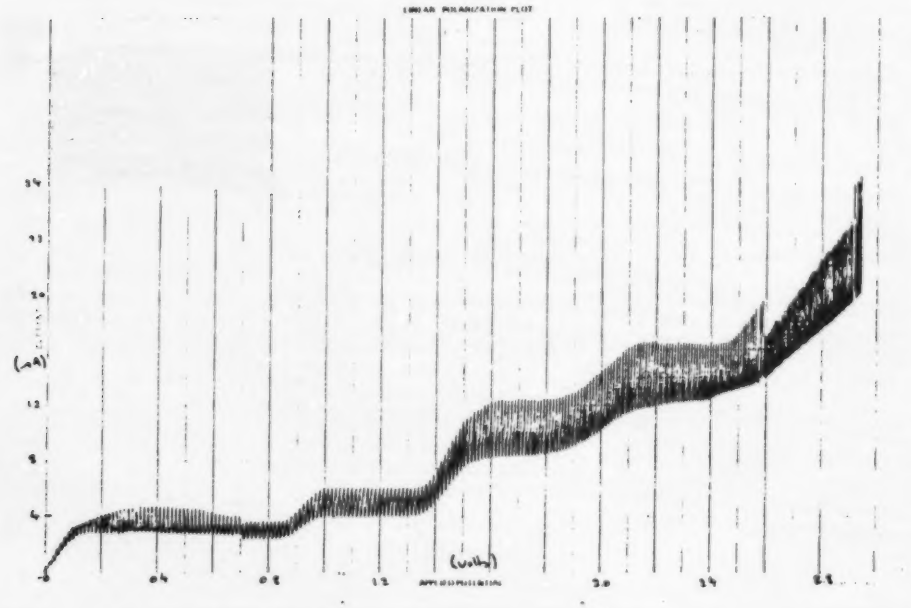

Figure A - (18): 0.003 M Cd, 0.0052 M Cu and 0.0051 M Zn solution, suppressed.

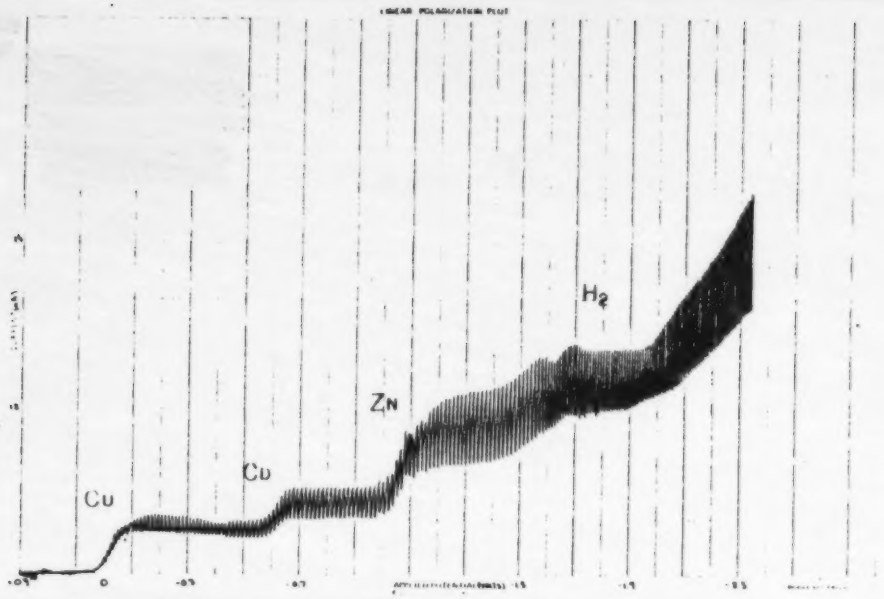


Figure A - (19): 2.97 x $10^{-4}$ M Cd, 5.10 x $10^{-4}$ M Zn, 5.23 x $10^{-4}$ M Cu solution, suppressed, versus the $Cu/CuSO_4$ reference electrode.

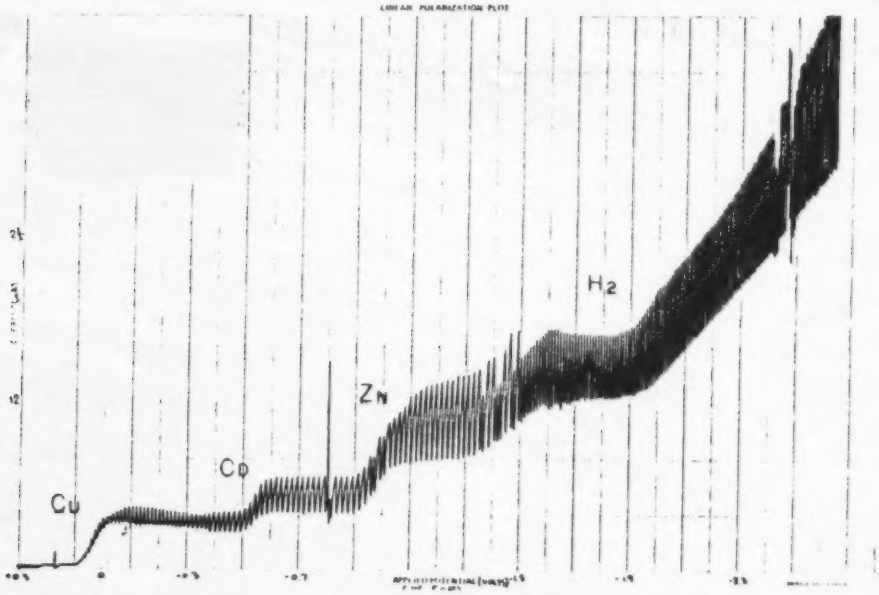


Figure A - (20): 2.97 x $10^{-4}$ M Cd, 5.10 x $10^{-4}$ M Zn, 5.23 x $10^{-4}$ M Cu solution, suppressed, versus the S. C.E. ($Hg_2 CL_2$).

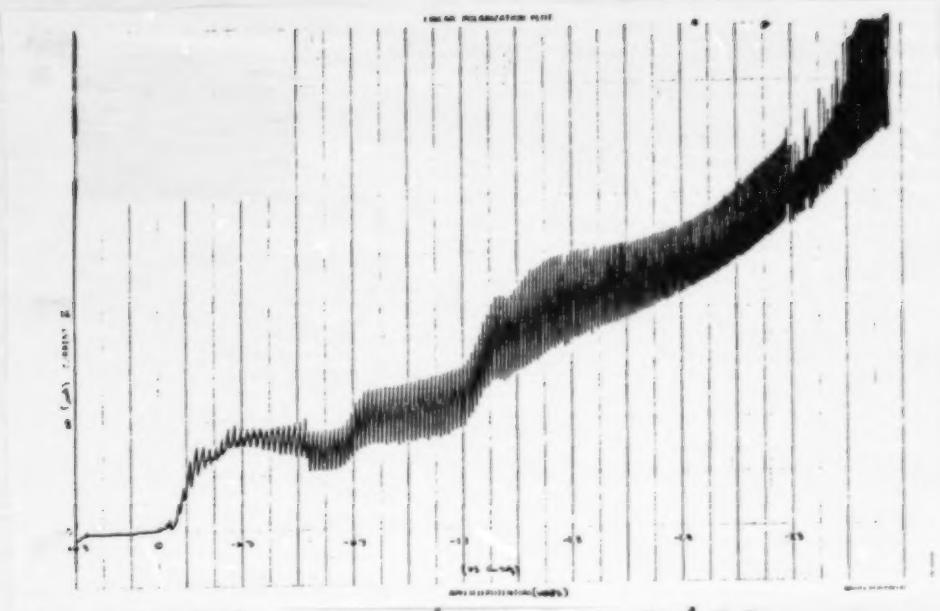

Figure A - (21): 2.97 x $10^{-4}$ M Cd, 5.10 x $10^{-4}$ M Zn, 5.23 x $10^{-4}$ M Cu solution, suppressed, aeration with compressed air.

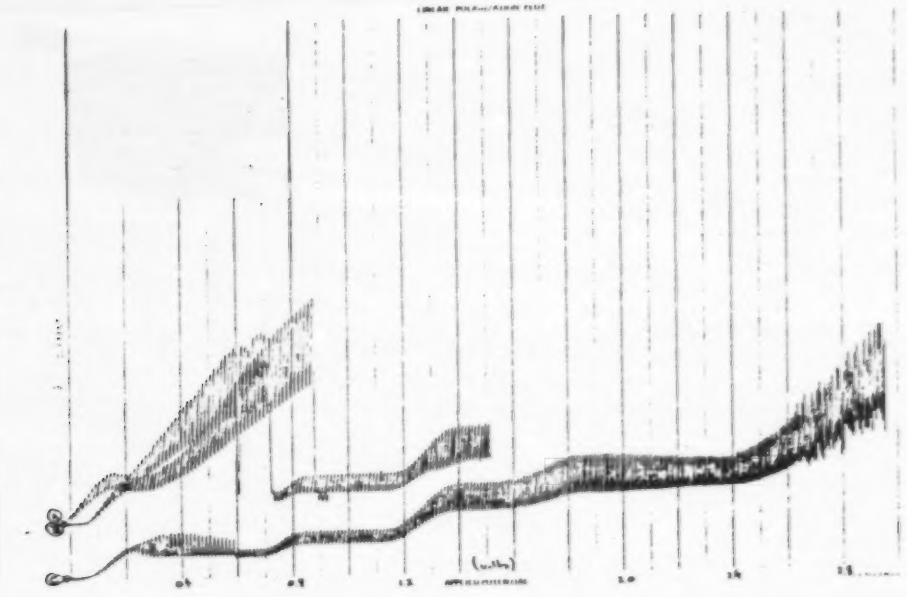

Figure A - (22): 0.003 M Cd, 0.0052 M Cu, 0.0051 M Zn solution, suppressed.

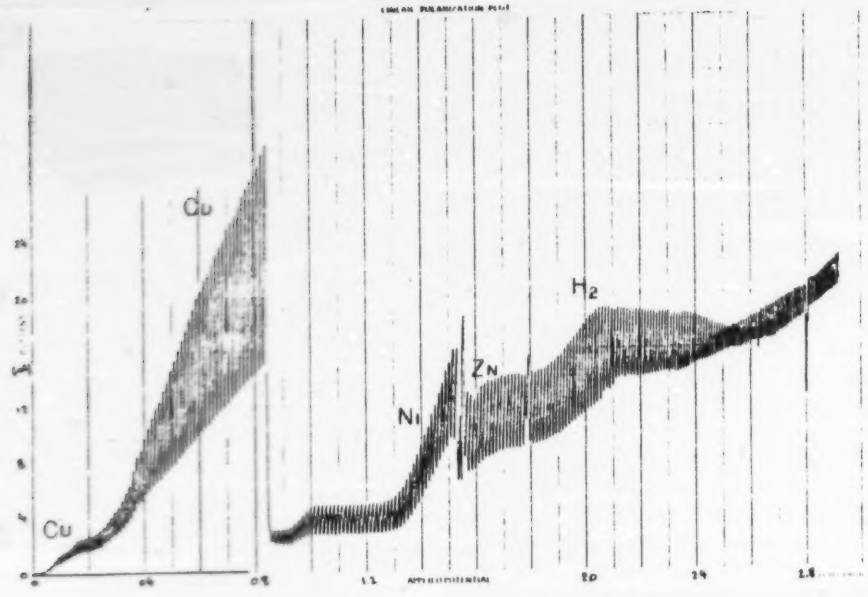


Figure A - (23): 2.20 x $10^{-4}$ M Cd, 3.90 x $10^{-4}$ Cu, 3.8 x $10^{-4}$ M Zn, 4.3 x $10^{-4}$ Ni, unsuppressed.

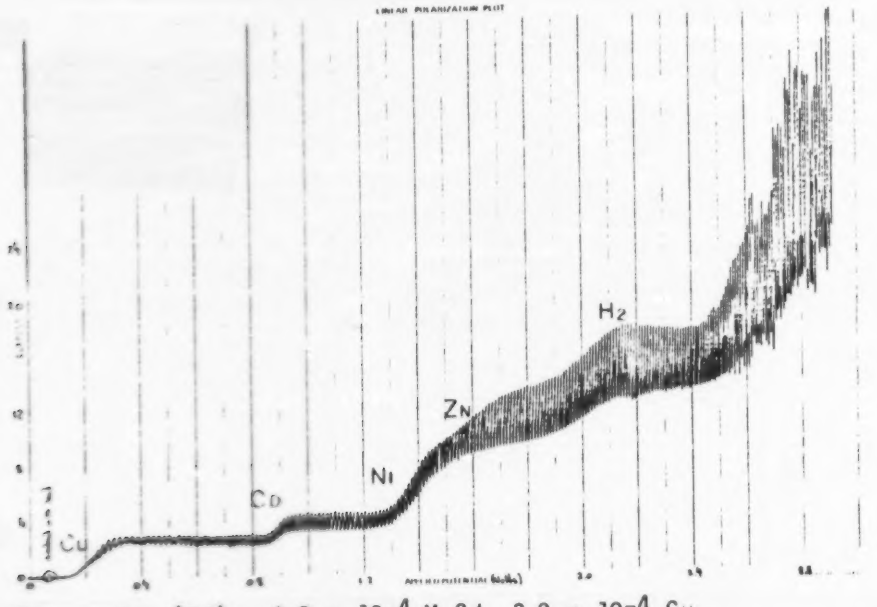


Figure A - (24): 2.2 x $10^{-4}$ M Cd, 3.9 x $10^{-4}$ Cu, 3.8 x $10^{-4}$ M Zn, 4.3 x $10^{-4}$ Ni, suppressed.

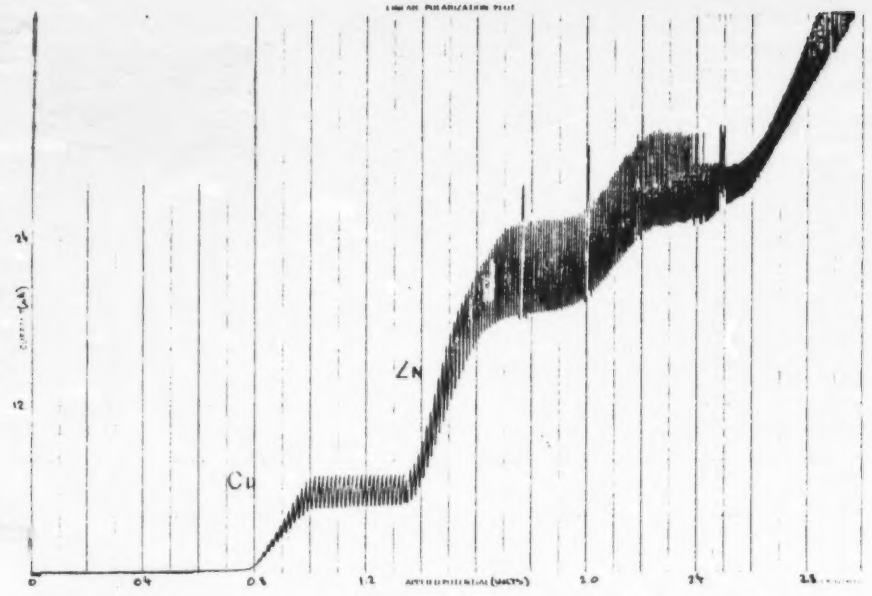


Figure A - (25): $8.9 \times 10^{-4}$ M Cd, $1.53 \times 10^{-3}$ M Zn solution ( 100 ppm), suppressed.

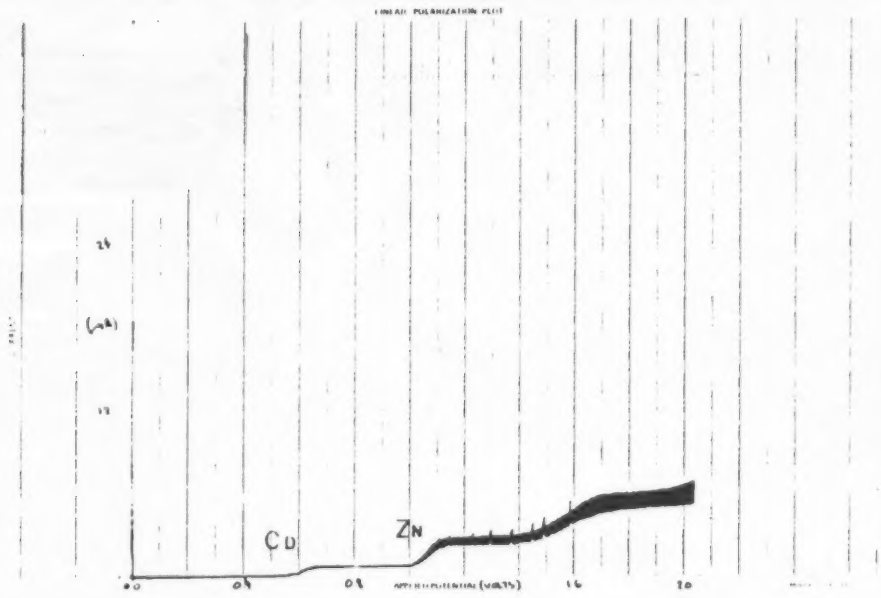


Figure A - (26): $8.9 \times 10^{-5}$ M Cd, $1.53 \times 10^{-4}$ M Zn solution ( 10 ppm), suppressed, versus $Cu/CuSO_4$ reference electrode.

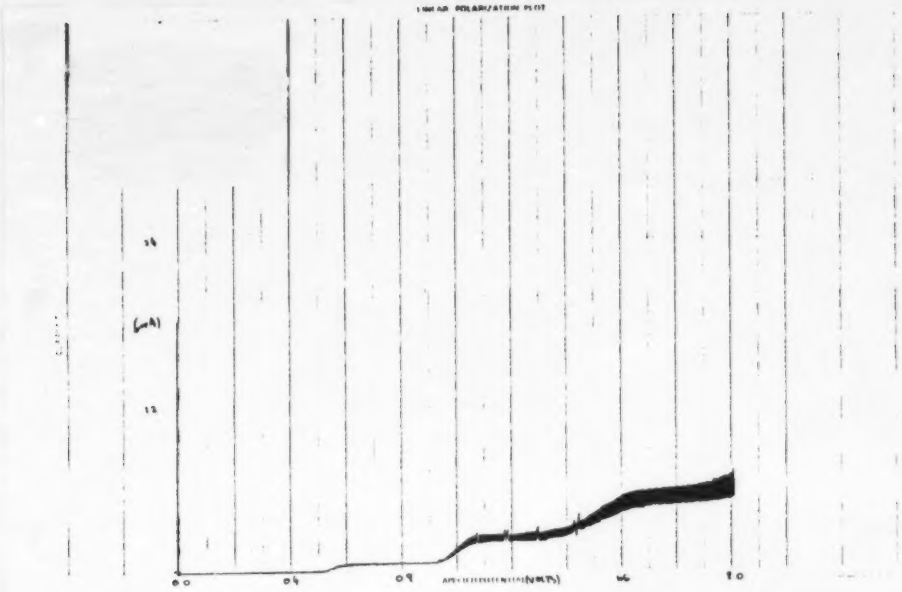

Figure A - (27): 8.9 x $10^{-5}$ M Cd, 1.5 x $10^{-4}$ M Zn solution, suppressed, versus $Hg_2Cl_2$ reference electrode.

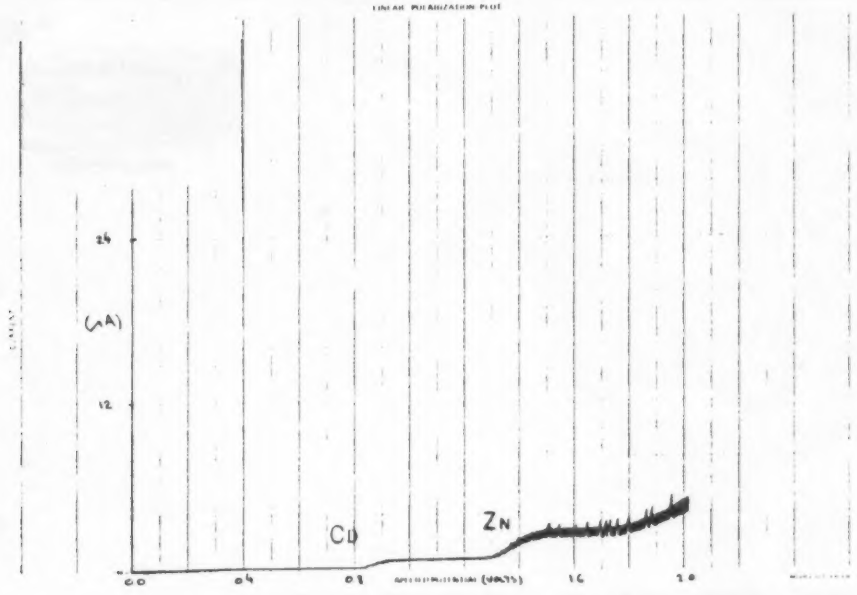


Figure A - (28): 8.9 x $10^{-5}$ M Cd, 1.5 x $10^{-4}$ M Zn solution, suppressed, versus Hg $SO_4$ reference electrode.

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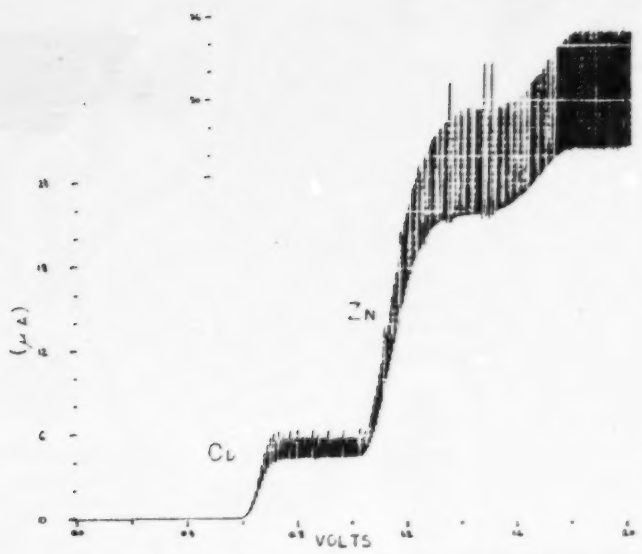


Figure A - (29): 8.3 x $10^{-4}$ M Cd, 1.8 x $10^{-3}$ M Zn solution ( 100 ppm), suppressed, versus $Cu/CuSO_4$ reference electrode.

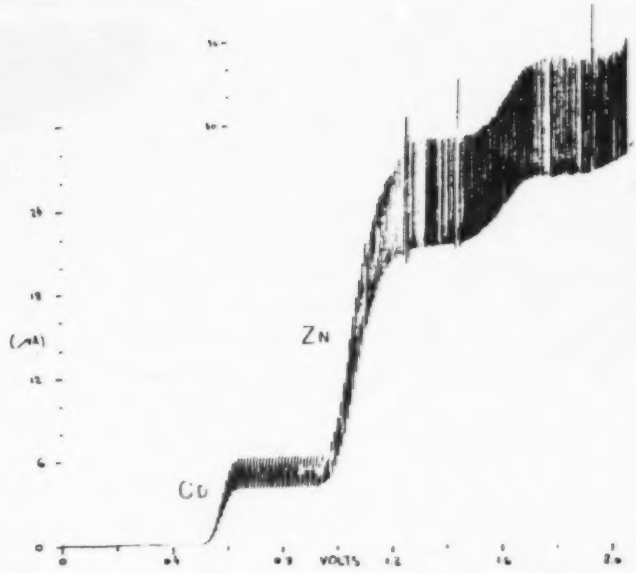


Figure A - (30): 8.3 x $10^{-4}$ M Cd, 1.8 x $10^{-3}$ M Zn solution, suppressed, versus $Hg_2CL_2$ reference electrode.

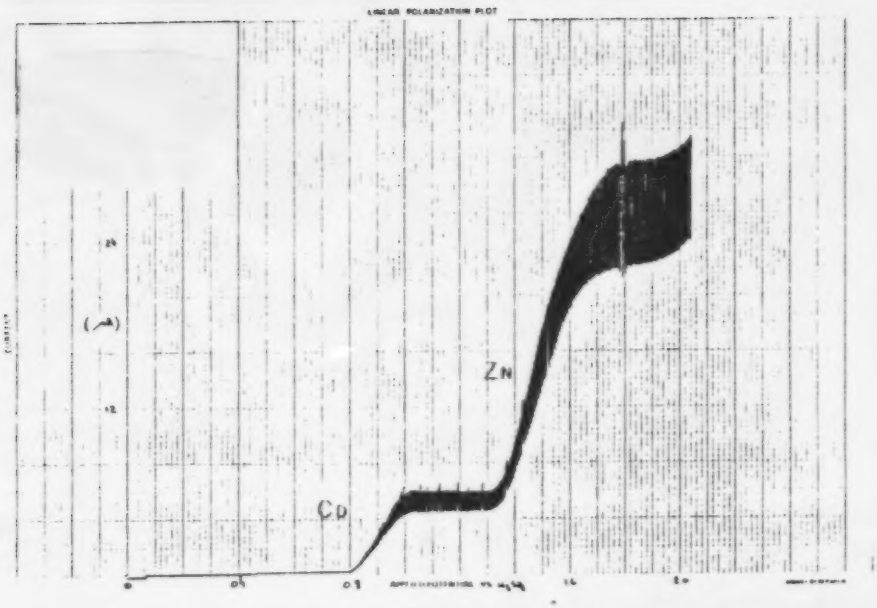


Figure A - (31): 8.3 x $10^{-4}$ M Cd, 1.8 x $10^{-3}$ M Zn solution, suppressed, versus $HgSO_4$ reference electrode.

## APPENDIX B

## SOLID ELECTRODE POLAROGRAMS

### Tests 1-2

Tests were run to study the plating characteristics of 3003-F solid aluminum cathodes. The cathode had the following dimensions:

length = 12.736 mm

diameter (d) = 9.524 mm

diameter (dm) = 3.3 mm

The exposed surface area of the right cylindrical surface was:

$$A = 2\pi r^2 + 2\pi rh - \pi r^2 = 5.15 \text{ cm}^2$$

As one can see by comparing the two polarograms, the increase in concentration does alter the shape of the current potential curve. Although the half-wave potential does not vary significantly, the height of the current wave is increased at the higher concentration.

### Tests 3-5

The following half-wave potentials have been determined from these plots:

| Cathode Reference | Dropping Hg $Cu/CuSO_4$ | Solid Al $Cu/CuSO_4$ | Dropping Hg $Hg_2Cl_2$ | Solid Al $Hg_2Cl_2$ | 430SS $Hg_2Cl_2$ |
|---|---|---|---|---|---|
| Cd | -0.65 | -0.82 | -0.56 | -0.76 | -0.76 |
| Zn | -1.17 | -1.13 | -1.00 | -1.14 | -1.10 |

Test 6

This blank test of deionized water was run to detect any stray currents in the potentiometric scan. The fact that the current stayed close to zero indicates that with the exception of $H_2$ evolution there are none.

Tests 7-8

These potentiodynamic scans show both plating and stripping curves. Plating involves the deposition of metal on the cathode as the potential moves to the right along the x axis. Stripping occurs when the direction of the scan is reversed and metal ions come off the cathode and back into solution. Note that the dip in the stripping curve corresponding to the dissolution of cadmium occurs at a lower potential than the plating of that same metal.

Tests 9-10

Note that with steel electrodes at potentials more anodic than -0.70 volts a substantial positive current is developed. This is due to corrosion of iron at the cathode. The effect of mixing seems to be an increase in the current at a given potential either in the anodic or cathodic direction. Note that the two lines cross at -0.70 volts in figure (10).

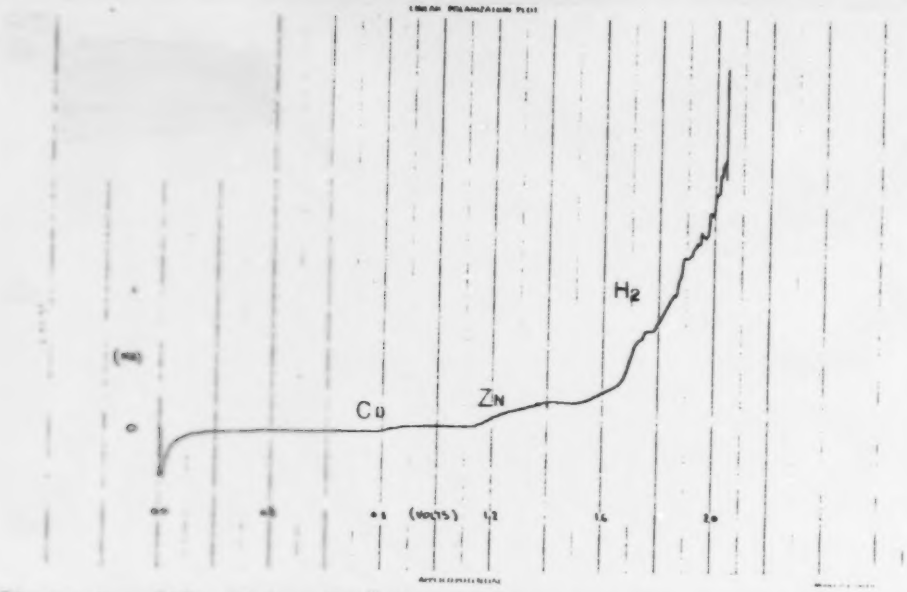


Figure B - (1): $8.9 \times 10^{-5}$ M Cd, $1.5 \times 10^{-4}$ M Zn solution, unsuppressed, with a 3003-F Al cathode and Cu/CuSO 4 reference electrode.

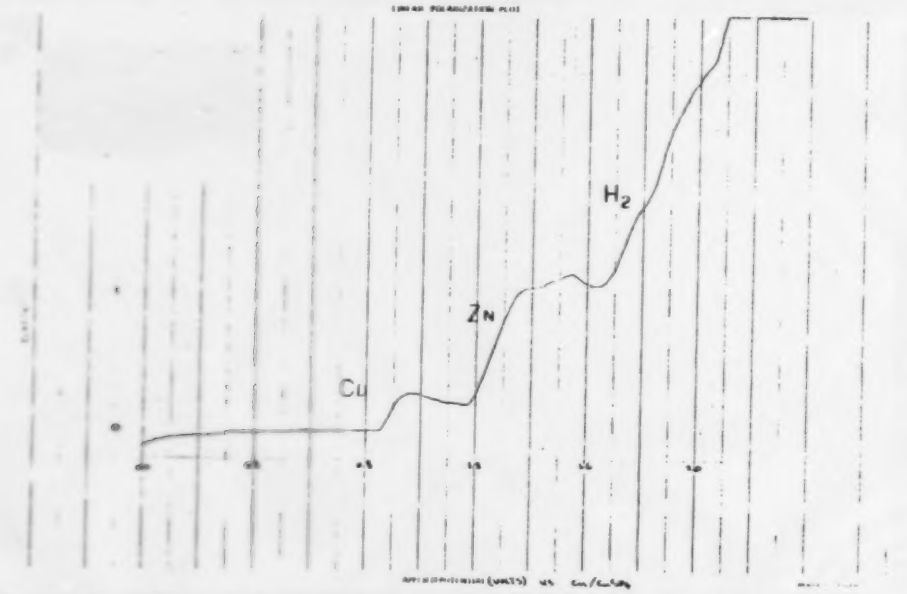


Figure B - (2): $8.9 \times 10^{-4}$ M Cd, $1.53 \times 10^{-3}$ M Zn solution, unsuppressed, with a 3003-F Al cathode and Cu/$CuSO_4$ reference electrode.

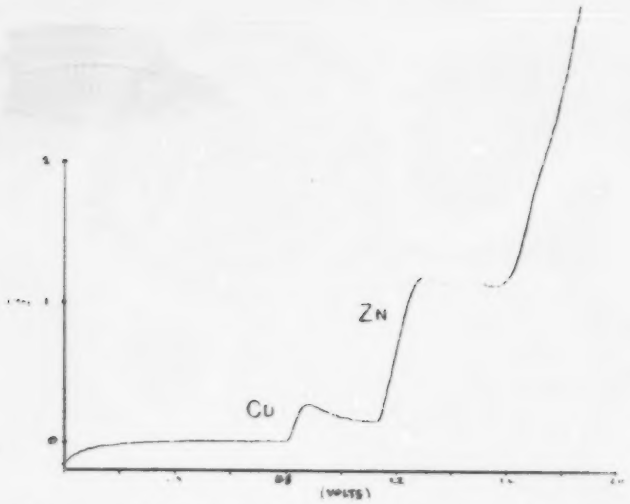


Figure B - (3): $8.3 \times 10^{-4}$ Cd, $1.8 \times 10^{-3}$ M Zn solution, with a 3003-F Al cathode and a $Cu/CuSO_4$ reference electrode.

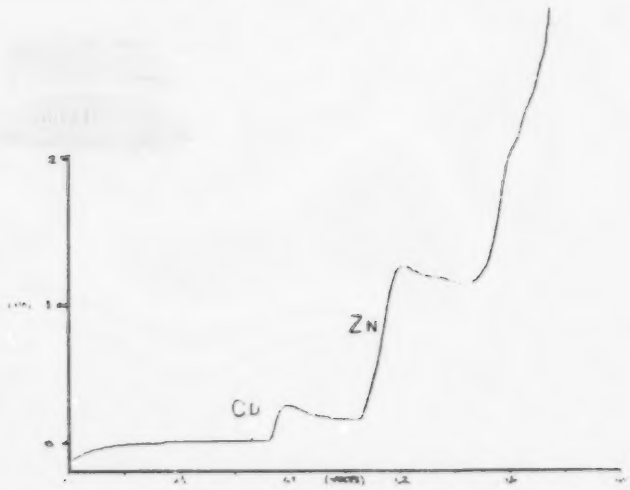


Figure B - (4): $8.3 \times 10^{-4}$ Cd, $1.8 \times 10^{-3}$ M Zn solution, with a 3003-F Al cathode and a $Hg_2Cl_2$ reference electrode.

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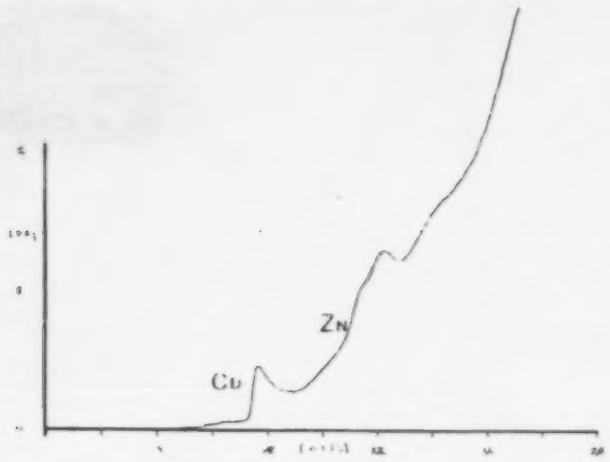



Figure B - (5): 8.3 x $10^{-4}$ Cd, 1.8 x $10^{-3}$ M Zn solution, with a 430SS cathode and a $Hg_2Cl_2$ reference electrode.

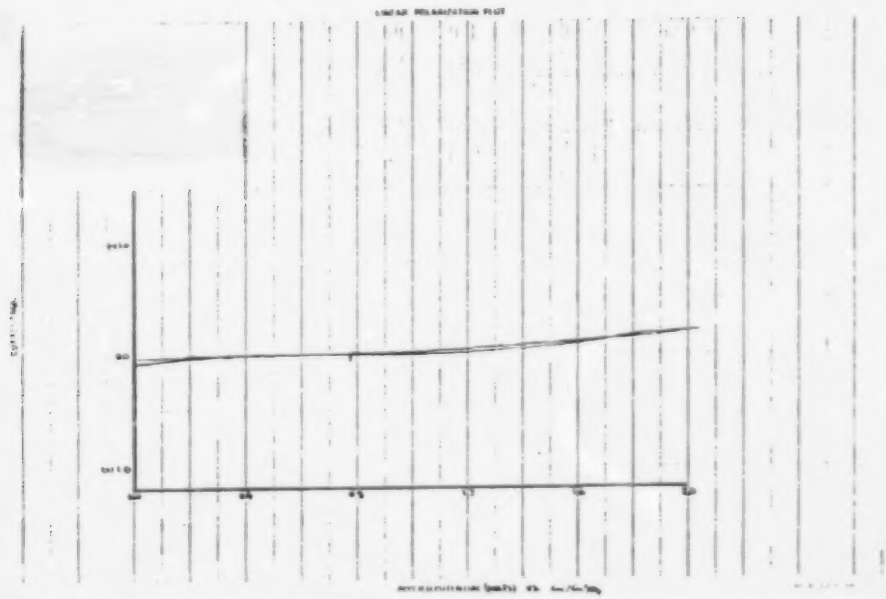


Figure B - (6): $SO_4$ blank run using deionized water adjusted to a pH of 4, with a 3003-F Al cathode and a $Cu/CuSO_4$ reference.

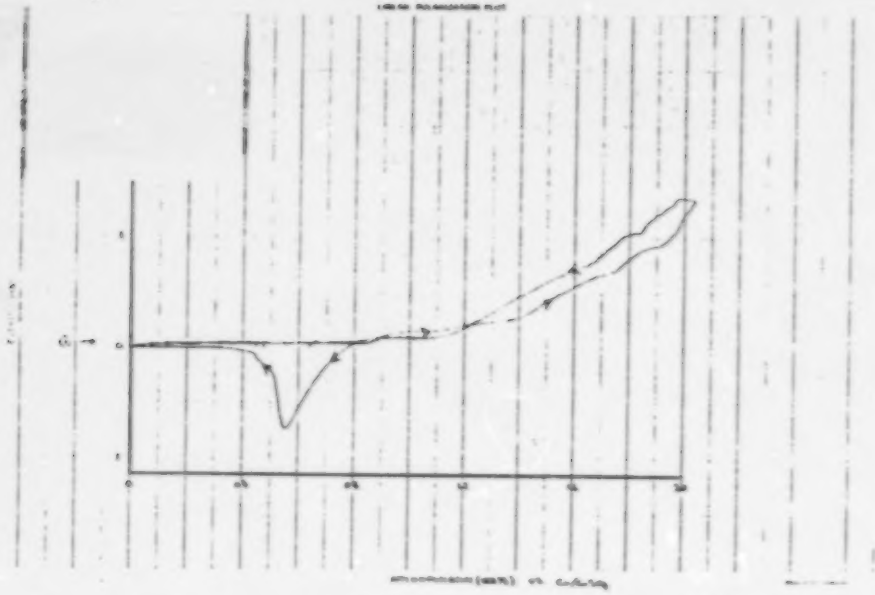


Figure B - (7): $4.45 \times 10^{-4}$ M Cd solution ( 50 ppm), with a 3003-F Al cathode and a $Cu/CuSO_4$ reference electrode.

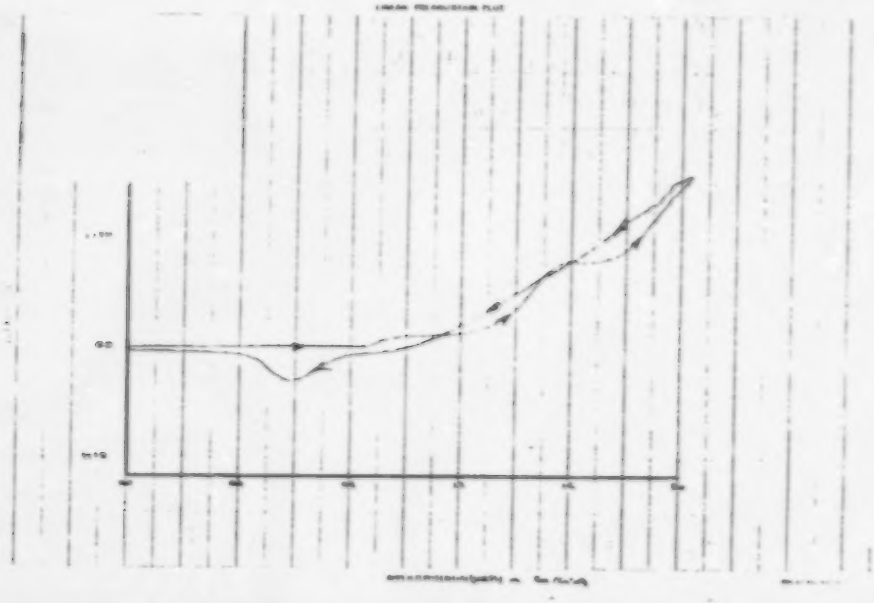


Figure B - (8): A rerun of test (7) using the same solution and electrodes.

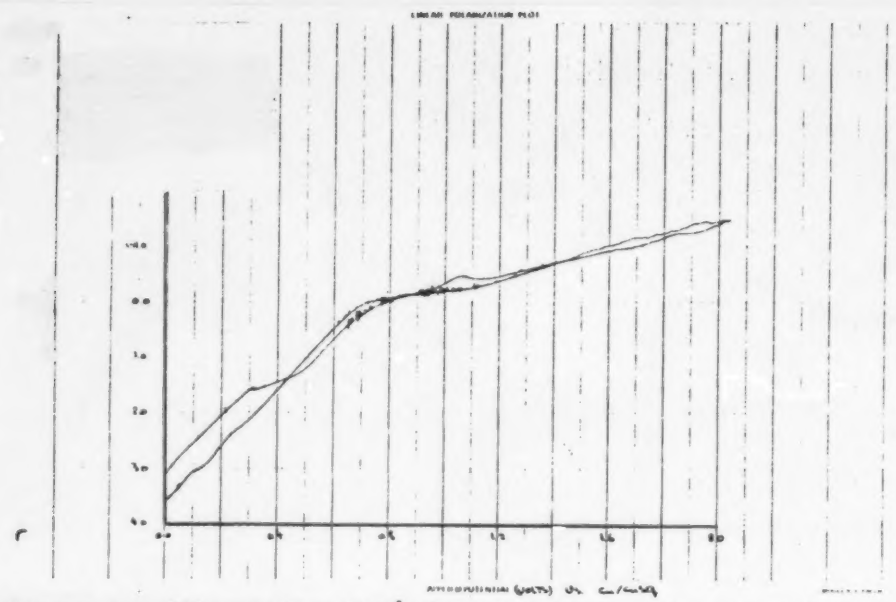


Figure B - (9): 4.45 x $10^{-4}$ M Cd solution, with a 1018 C.R. - C.S. cathode and a $Cu/CuSO_4$ reference electrode.

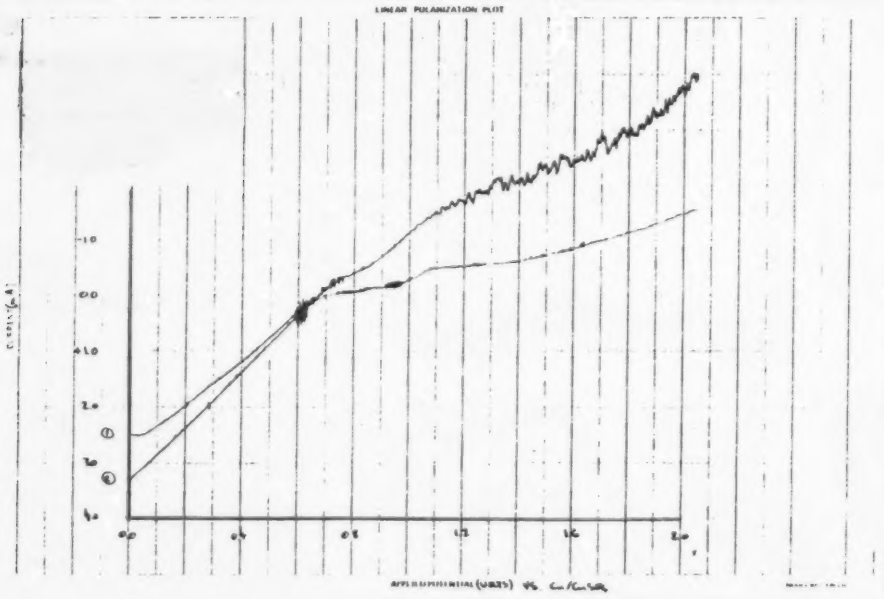


Figure B - (10): 4.45 x $10^{-4}$ M Cd solution, with a 1018 C.R. - C.S. cathode and a $Cu/CuSO_4$ reference electrode. Two runs, with and without solution mixing.

APPENDIX C

PLATING STUDIES

Plating Test I

A test was run to check the plating solution before running a long-term plating test. This two component solution contains 93 ppm Cd and 98 ppm Zn, or approximately 8.3 x $10^{-4}$ M Cd/1.5 x $10^{-3}$ M Zn. The pH was adjusted to 4 with dilute $H_2SO_4$. Forty milliliters of solution, suppressed with 28 drops ( 0.7 ml) of 0.2% gelatin solution, was deaerated with nitrogen for twenty minutes. A polarographic scan was then run from 0.00 to -2.00 V vs. Hg $SO_4$. The initial mercury drop rate was 4.42 seconds. The scan rate was 1.9 mn/sec. The current following output was conditioned with an RC network, TC = 1 sec.

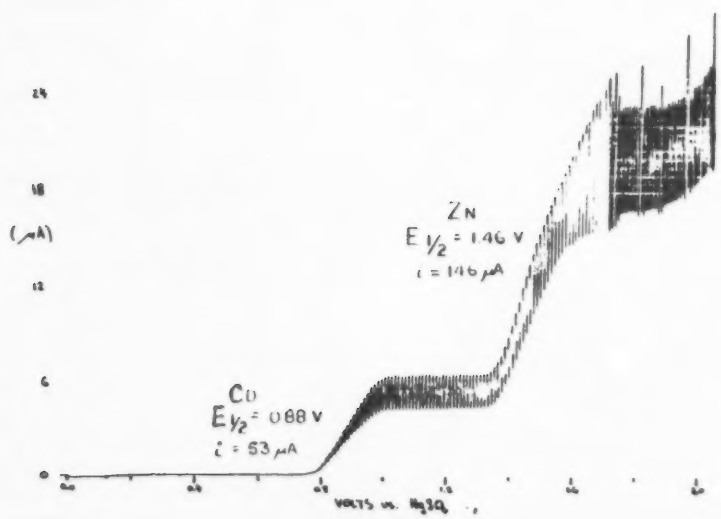



Figure C-1 Plating Solution Check

A potentiostatic test was run to study the plating rate of Cd from bimetal solutions. Solution 14,487-91-I, containing 93 ppm Cd and 98 ppm Zn, was the test environment. The pH=4. An aluminum cathode, 3003-F, with an exposed surface area of 5.0 $cm^2$, was used with graphite anodes. The open-circuit potential of the aluminum, in this solution, was $E_{corr}$ = -0.76V vs. Cu-$CuSO_4$. The applied potential was -0.80V vs Cu-$CuSO_4$.

An attempt to correlate stirring speed and current density failed due to the effect of increasing surface area. The surface of the cathode started to plate immediately; the deposit was dark, charcoal gray when wet. After 54 minutes, the stirrer setting was set at minimum and left there for the remainder of the experiment, since this was not a controlling variable. At this time the surface of the cathode was covered by a gauze-like deposit with an extremely fuzzy surface. The current increased as the surface deposit continued to grow in area.

As large portions of this gauze-like coating would detach or partially detach, appropriate changes in the current density were noted, some of these transients had extremely large absolute magnitudes.

The test was allowed to run overnight. Some of the deposits which had broken away from the surface were circulating in the solution. Rapid redissolution did not occur. The following morning it was discovered that large increase in surface area, overnight, had driven the recorder off scale for approximately 2 hrs. and 24 minutes. A much larger quantity of solid metal was circulating in the solution and the presence of some carbon was evident. The nature of the surface deposit on the cathode had changed. The coating was much denser, large pores open through the coating to the electrode surface were visible. The coating itself was nodular in appearance, the outer portion being less dense and somewhat fuzzy. Portions of the lower layer, appeared to have formed or nucleated into small round balls with highly reflective surfaces. The test was shutdown after 22 hours and 48 minutes.

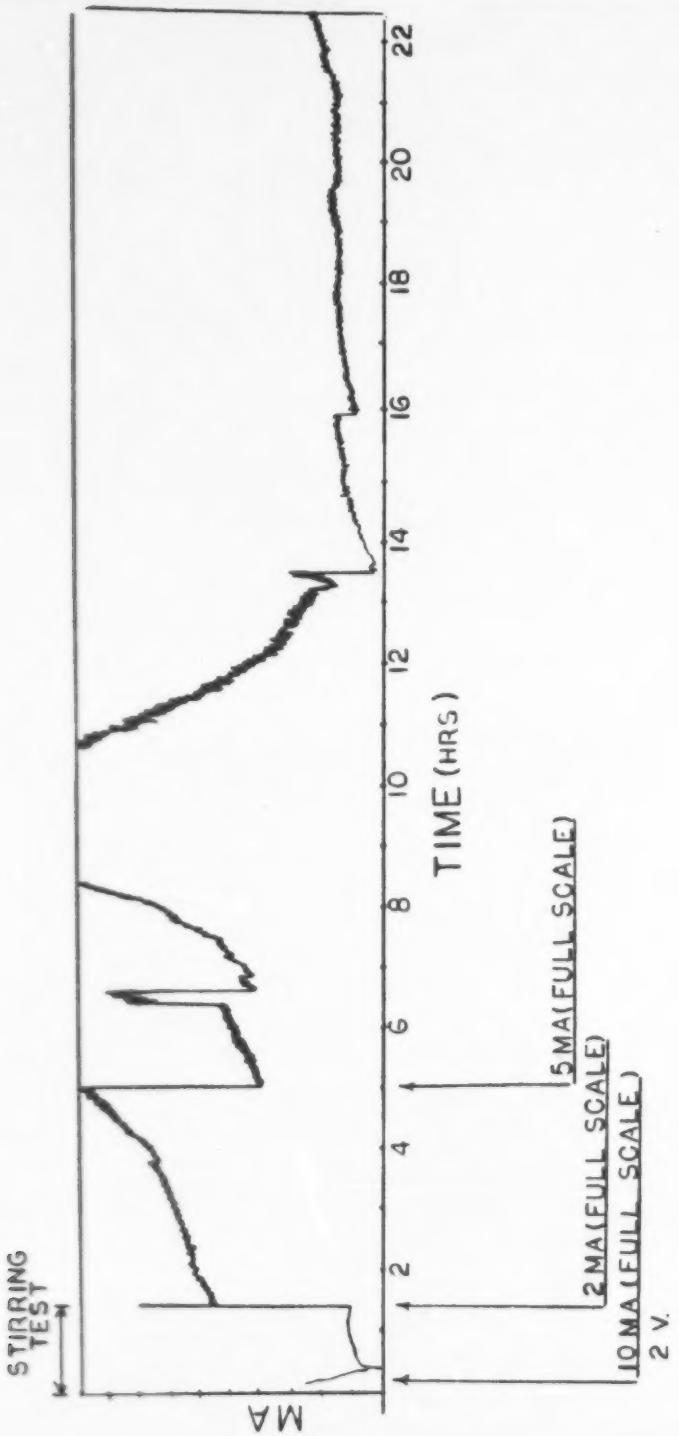
The supernate was filtered through #41 ashless filter paper. The solution had the coloring of lightly made tea. This is assumed to be due to the dissolution of graphite. The anodes were noted as being effected. All but 3 ml. of solution was accounted for. The cell originally contained 750 ml.

The solids were washed out of the cell with deionized water and collected in a second sheet of #41 ashless paper. After a photograph was taken, the cathode deposit was also washed into this filter paper. Some abrasion was necessary to free the deposit.

The pH of the filtered solution was 2.9.

Approximately 40 ml. of test solution No. I and 28 drops (0.72 ml) of gelatin suppressor were deaerated with nitrogen for twenty minutes. A Polarographic scan was then run from 0.00 to 2.00 volts vs $H_2SO_4$. The solution pH was 2.9.

Figure C-2 Plating Test No. I



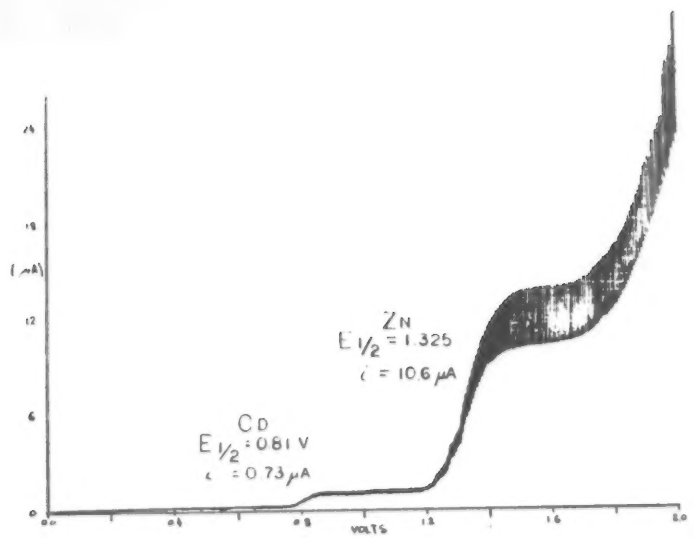



Figure C-3 Final Polarograph for Test I

Plating Test II

A Potentiostatic plating test was performed to study the plating rates and characteristics of Zn and Cd from the two component standard solution (93 ppm Cd/98 ppm Zn) no. 14,487-91-I. An 3003-F aluminum cathode was used with two graphite anodes. The solution was deaerated with nitrogen and stirred, (stirring setting No. I). The initial pH ~ 4 ($H_2SO_4$). The open-circuit potential of the aluminum in this solution was $E_{corr}$ = -0.76V and the applied potential was -1.45 V vs. Cu-$CuSO_4$.

The run was started at 3:00 p.m. on 2/11/81. The current rose from a low initial value ( $\geq$2.5 mA), due to the agitation of the nitrogen bubbles, to 47 mA after stirring for four hours. The current increased slowly over the next 13 hours and 40 minutes to 48.8 mA. The unit was then shut down. Total time of the run was 17 hrs. and 40 minutes.

The solution contained a large amount of graphite. Much more than plating test I, No. 14,487-93. Unlike the previous run, however, the metal appears to have adhered to the cathode. There are no large deposits of metal in the solution. The solution was filtered through #41 ashless paper and set to the laboratory for analysis. A polarograph of the solution was run. The solids on the cathode were removed by abrasion and washing and sent for analysis also.

In the current and potential chart illustrated in figure the current ranges between 0-100 ma (full scale) while the voltage ranges between 0-2 volts (full scale). The initial solution pH was 4 and the electrolyte was deaerated for twenty minutes with cylinder nitrogen prior to the start of the run. The chart speed of figure C-4 was 5 cm/hour. The reference electrode was Cu/$CuSO_4$.

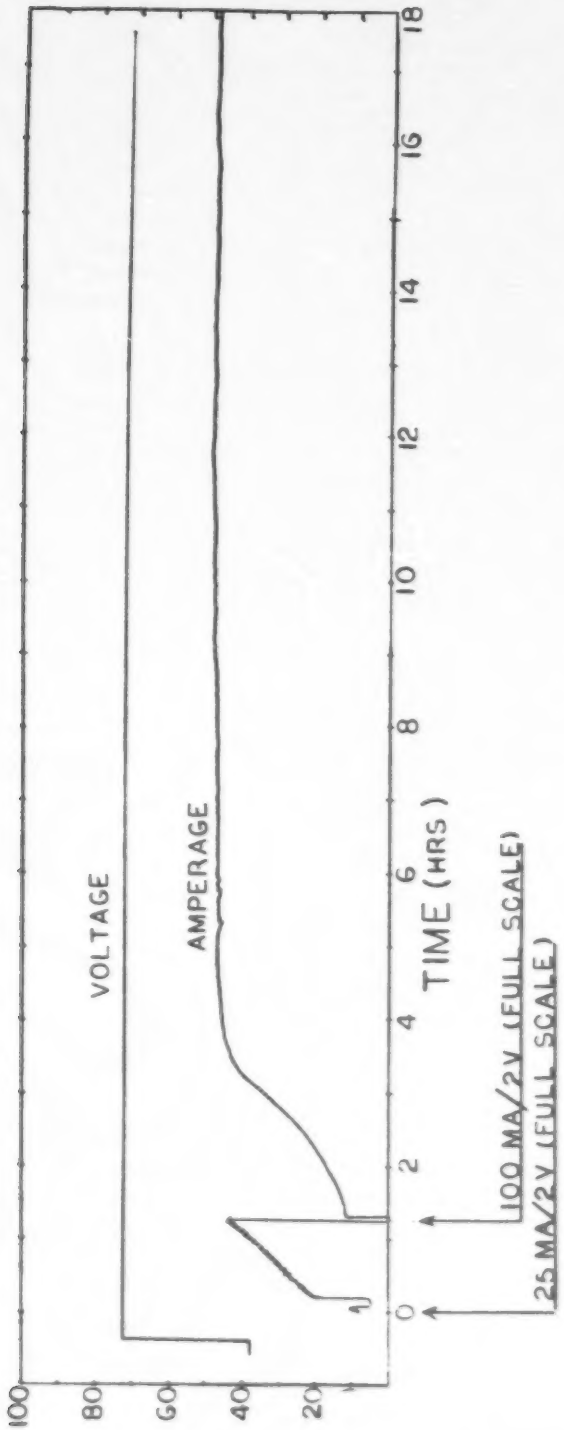
The dimensions and surface area of the cathode utilized for this plating study were as follows:

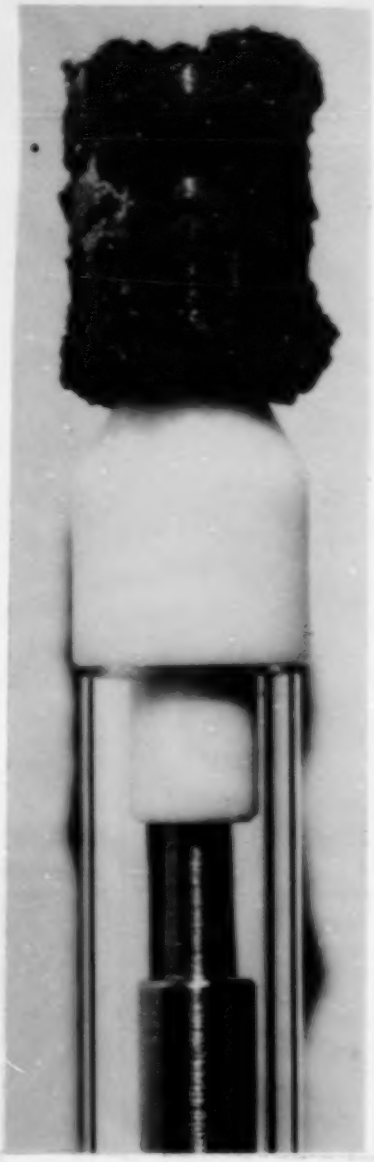
d = 0.9536 cm
h = 1.2716 cm
dm = 0.508 cm  m = masked area

$A = 2\pi r^2 + 2\pi rh - \pi r_m^2$
$A = 5.04\ cm^2$

Figure C-5 shows a photograph of the cathode after the completion of potentiostatic plating test II. The pores were approximately 0.08 cm in diameter and the cathode surface visible through them. Shiny flecs of metal seemed to be embedded in the surface coating which was "hard" and had to be removed from the aluminum substrate with a teflon spatula. The cathode/deposit interface was not particularly adherent. Approximately 0.181 grams of material was recovered in this manner.

Figure C-4 Plating Test No. II





Test I
magnification 3.5x

Test II
magnification 3.5x

Figure C-5 Solid Electrode Deposit

A polarograph was run to determine the amount of metals removed from solution by plating in Test II. Approximately 40ml. of solution and 28 drops (0.72 ml.) of suppressor were placed in the cell and deaerated for twenty minutes. The scan was then run from 0.00 to 2.00 volts vs. $HgSO_4$.

The half-waves appear to have shifted noticeably. The Cd wave appears at $E_{1/2}$ = -0.58V and the Zn at $E_{1/2}$ = -1.30V vs. $HgSO_4$. The final solution Ph was 2.5. The Cd level could not be determined without increasing the sensitivity. The Zn had decreased to $i_d$ = 1.25 $\mu$A or ~13 ppm.

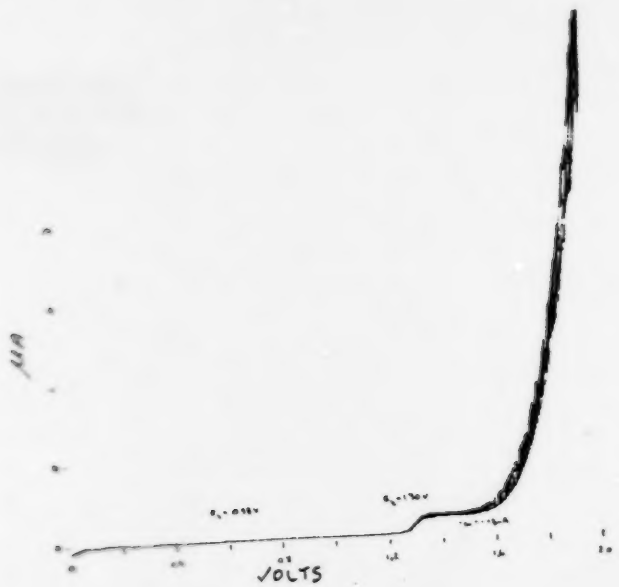



Figure C-6 Final Polarograph Test II

Plating Test III

Approximately 46 ml. of solution and 28 drops (0.7 ml.) of gelatin (0.2%) were used per test. The solutions were deaerated for twenty minutes prior to the start of each scan. The scan rate was 1.9 mv/sec. An RC network consisting of an 1 megaohm resistor and a 0.1 μf capacitor were employed to dampen the current, voltage follower, output of the potentiostat.

I.) 20 ppm standard solution - contains 19.6 ppm Cd and 19.3 ppm Zn, pH~4($H_2SO_4$)

II.) 40 ppm standard solution - contains 39 ppm Cd and 39 ppm Zn, pH~ 4($H_2SO_4$)

III.) 80 ppm standard solution - contains 80 ppm Cd and 78 ppm Zn, pH = 4($H_2SO_4$)

IV.) Mass Balance (Glassware) Test Solution

A one liter Princeton Applied Research Corrosion cell was used to demonstrate that a mass-balance could be achieved using the Magnar Potentiostat. The cell was deaerated with nitrogen and stirred with a magnetic stirrer. The solution was prepared from sulfate salts, the nominal concentrations were 100 ppm Cd and 100 ppm Zn. The cell was filled with 200 ml of solution. The control potential was 1.45V vs. Cu-$CuSO_4$. The cell was run for approximately 2 1/2 hours, with currents in excess of 100 ma being noted. A large amount of material was obviously plated. The plate was porous, and not particularly adherent to the substrate. Large amounts of material had broken away from the surface and were circulating in the solution.

The test solution was filtered through #41 ashless paper. The cathode was then cleaned by abrasion and this material was also washed through the filler paper. Total mass collected after drying was 0.0760g. material.

Analysis by polarographic methods showed that the solution contained:
37.5 ppm Zn
28.5 ppm Cd

| | Cd. | Zn |
|---|---|---|
| Analysis of Initial Solution (90 Cd/95 ppm Zn) | 0.090 g. | 0.095 g. |
| Analysis of Final Solution (26 Cd/55 Zn) removed | 0.026<br>0.064 g. Cd | 0.055<br>0.040 g. |

total removed
0.104 g. x 0.7 l. = 0.0728 g.

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Figure C-7 20 ppm Standard Solution

Figure C-8 40 ppm Standard Solution

Figure C-9 80 ppm Standard Solution

Figure C-10 Glassware Mass Balance

Plating Test IV - Aluminum Anode Test

A potentiostatic plating test was performed to study the applicability of aluminum electrodes, as anodes, in the large demetalization test facility.

Three electrodes of 3003-F aluminum were used as the cathode (1) and anodes (2). The surface area of each was 5.0 $cm^2$. The test solution was nominally 93 ppm Cd and 98 ppm Zn, pH = 4 ($H_2SO_4$). The volume of solution was 750 ml. The solution was deaerated and stirred.

The specimen appeared to be plating, at the edges, after 2 minutes at potential. The applied potential was -1.45 V vs. Cu-$CuSO_4$. After twenty minutes the current started to drop due to the corrosion of the anodes. After approximately one hour, the output of the potentiostat was overloaded. The unit was switched to high voltage mode and the current immediately started to increase. A total voltage of -58.3 volts was needed to maintain the applied voltage of -1.45 volts. This increased to > 60 volts at the maximum current density and decreased to approximately 39 volts at the end of the test. At the one hour mark it was obvious that there was promoted growth of bulk film on the anode surfaces. Also, there were small areas of highly promoted general attack, crevicing, on the anode surface.

A plot of the current and applied voltage versus time is given as figure (C-11) Again the voltage scale was 0-2 volts (full scale) while the current was 0-100 ma (full scale). The chart speed was again 5 cm/hour and the run lasted 28.52 hours. The weight of metal recovered from the cathode was 0.42 grams and the total current determined by integration of the area under the current line in figure (C-11) was 1641 coulombs.

The deposit on the cathode resembled the deposit shown in figure (C-5) for test II with the exception of whitish aluminum oxide formations or bloom on the upper edge surfaces.

A polarographic scan was run to determine the amount of Cd and Zn remaining in solution after 28 1/2 hours.

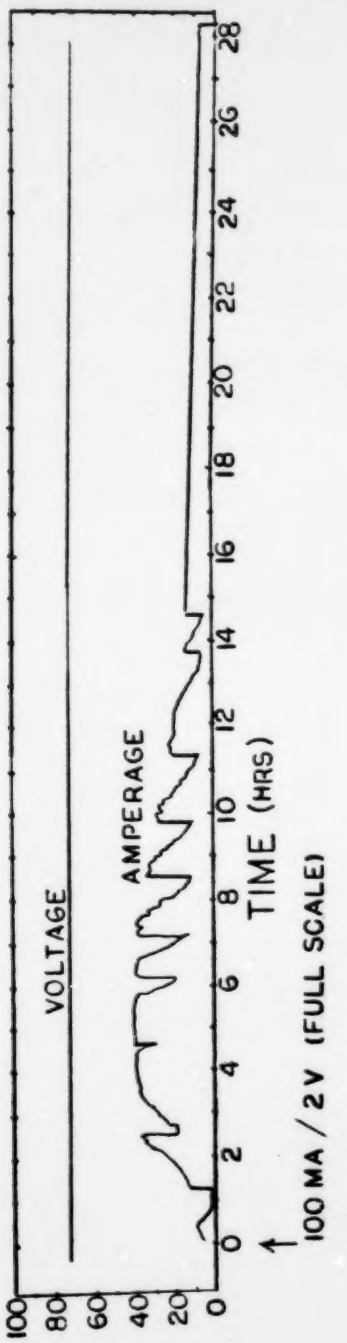
The scan was run from -0.00 volts to -2.00 volts vs Cu-$CuSO_4$. The solution was suppressed with 28 drops (~.7 ml) of 0.2% gelatin solution. Solution pH = 4.3.

The test solution was filtered through 41 ashless filter paper. After filtering, all but 14 ml. of the initial solution was recovered.

Atomic Absorption Analysis: (3-11-81) pH = 4.3

| | Solution | Solid |
|---|---|---|
| Cd | 0.3 ppm | 61,000 mg. |
| Zn | 2.17 | 17,000 mg. |
| Al | 28 60,000 mg. | |
| | 4 mg. Pb. | |

Figure C-11 Plating Test IV - Aluminum Anode



analysis of initial solution (17-I)

| | |
|---|---|
| Cd | 88 ppm |
| Zn | 100 |

Plating Test V - Lead Anode

A potentiostatic plating test was run to study the applicability of sulfated lead anodes in the demetalization process. The one liter test cell contained 670 ml. of stock solution (17-I), initially. The applied potential was -1.45 volts vs. a Cu-$CuSO_4$ reference. The test was started at 4:07 P.M. on 3/3/81 and run for 24 hours. The solution was deaerated and stirred. The cathode was exposed in the deaerated solution for approximately 20 minutes prior to the start of the test.

After 15 hours large pieces of porous-structured metal plate were floating in the solution. Gas bubbles entrained in and on the porous structure accounted for the buoyancy. When the cathode was removed from solution at the end of the test, the plated deposit dropped off en masse and floated in the solution.

After 24 hours, the solution was filtered and the solid weighted. They were then sent for analysis by atomic adsorption. All but 22 ml. of solution were recovered after filtration.

The plated surface achieved with the lead anodes did not have the mechanical adherence of that prepared using graphite anodes. The addition of graphite on the plated surface may have an effect on the quality of the plate.

The sulfated-lead surfaces of the anodes, which were initially charcoal black, had some areas of brownish discoloration.

Figure C-13 presents the current-potential versus time chart for the lead anode test. The voltage range on the chart is 0-2 volts (full scale) while the current range is 0-100 ma (full scale). The chart speed was 5 cm/hr with every major division on the plot equaling 1 cm. As mentioned before the applied potential was -1.45 volts versus the Cu/$CuSO_4$ reference electrode and the open circuit potential -0.77 volts. By integrating the area under the current curve a total current flow of 1221.3 coulombs may be calculated.

Atomic Absorption Analysis (3/11/81) pH = 2.7

| Initial Solution | | Final Solution | |
|---|---|---|---|
| Cd | 88 ppm | Cd | 4 ppm |
| Zn | 100 ppm | Zn | 71 ppm |
| | 0.126 g metal | | 0.05 g metal |

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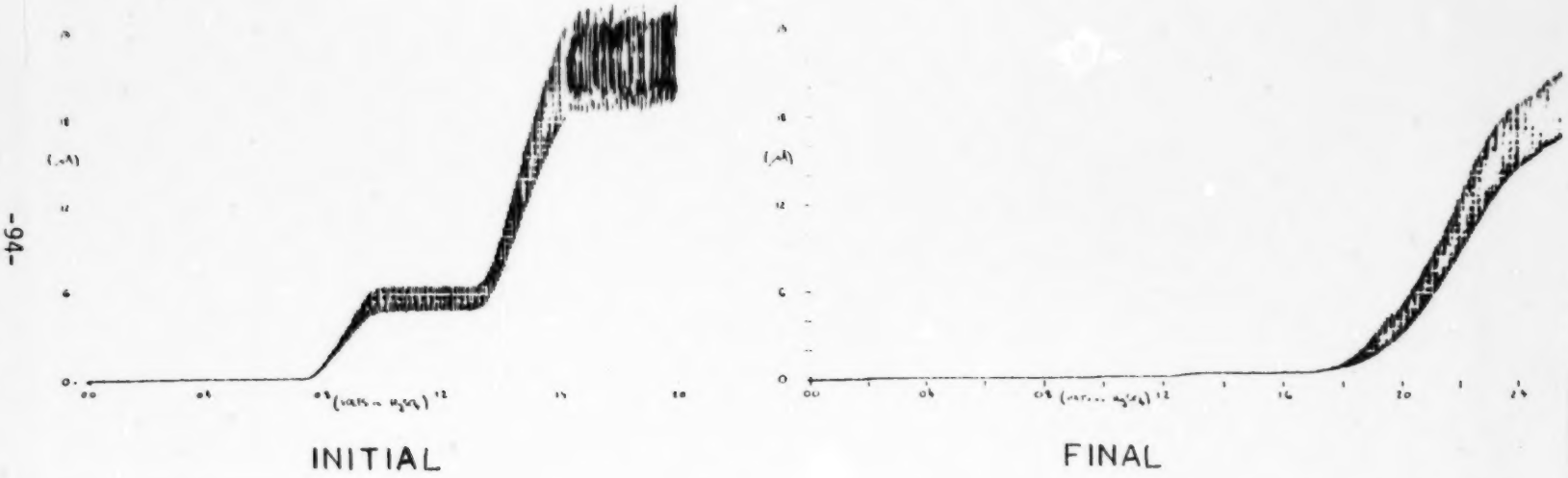
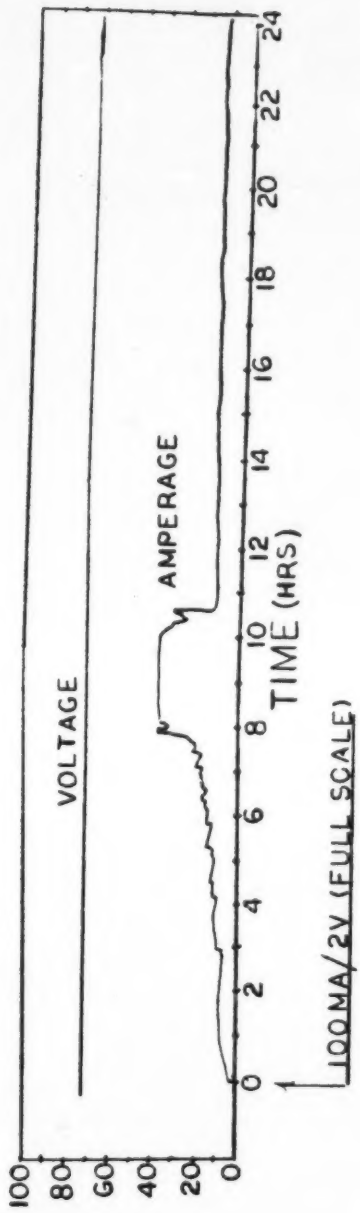



Figure C12 Polarographic Scan Of Test Solution IV

Figure C-13 Plating Test V-Lead Anode



Filter Solids (0.0694 g total weight)

| | |
|---|---|
| Cd | 52000 mg |
| Zn | 8300 mg |
| Pb | 310 mg |
| | 0.0606 g metal |

APPENDIX D

BENCH SCALE TESTS

SLUDGE DEMETALIZATION TEST 1 11-4-80

DATA

| Hours Operation | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Time | 9:26 | 10:26 | 11:26 | 12:26 | 1:26 | 2:26 |
| Air Flow (SCFH) | 5 | 5 | 5 | 4 | 5 | 5 |
| Sludge Flow (l/min) | 16.44 | 15.96 | 15.84 | 16.08 | 16.20 | 16.2 |
| Temperature (°C) | 27 | 44 | 52 | 57 | 56 | 54 |
| pH | 4.0 | 4.05 | 3.95 | 3.95 | 3.95 | 4.0 |
| Total Cell Voltage | 1.39 | 1.85 | 2.04 | 2.16 | 2.21 | 2.22 |
| Reference Voltage | 1.203 | 1.203 | 1.203 | 1.203 | 1.203 | 1.203 |
| Cell Amperage | - | 0.3 | 0.75 | 1.07 | 1.09 | 1.08 |
| Sample Volume (ml) | 0 | 254 | 252 | 250 | 250 | 250 |
| Reactor Volume (l) | 18.25 | 18.0 | 17.74 | 17.49 | 17.24 | 16.94 |

METALS ANALYSIS

MASS (μg)

| | | Cu | Zn | Pb | Ni | Cd | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| Sludge on Electrode | A | 1330 | 2500 | 1750 | 220 | 29 | 1300 | 24,000 |
| | B | 1570 | 3000 | 1800 | 190 | 33 | 1500 | 27,000 |
| | C | 1540 | 2650 | 1850 | 240 | 63 | 1500 | 35,000 |
| | D | 1700 | 2850 | 1900 | 240 | 39 | 1750 | 35,000 |
| Deposit on Electrode | A | 200 | 1560 | 1420 | 520 | 1100 | 176 | |
| | B | 210 | 1320 | 1800 | 480 | 580 | 180 | |
| | C | 300 | 2300 | 1600 | 260 | 630 | 220 | |
| | D | 230 | 1100 | 1120 | 420 | 170 | 200 | |
| Deposit on Graphite | | 110 | 500 | 420 | 43 | 78 | 180 | |
| Total (μg) | | 7080 | 17280 | 13240 | 2570 | 2644 | 6826 | 121,000 |

CONCENTRATION (mg/l)

| Sample | % TS | % VS | Cu | Zn | Pb | Ni | Cd | Cr | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 2.61 | 1.47 | 52 | 164 | 64 | 12 | 0.89 | 23 | |
| 1 | 2.47 | 1.39 | 50 | 160 | 74 | 11 | 0.93 | 33 | |
| 2 | 2.44 | 1.37 | 53 | 156 | 66 | 11 | 1.0 | 41 | |
| 3 | 2.45 | 1.38 | 46 | 135 | 57 | 10 | 0.85 | 44 | |
| 4 | 2.41 | 1.35 | 51 | 146 | 54 | 11 | 1.0 | 55 | |
| 5 | 2.44 | 1.37 | 50 | 143 | 53 | 11 | 0.96 | 63 | |
| F | 2.33 | 1.31 | 47 | 141 | 63 | 11 | 0.96 | 63 | |

OBSERVATIONS

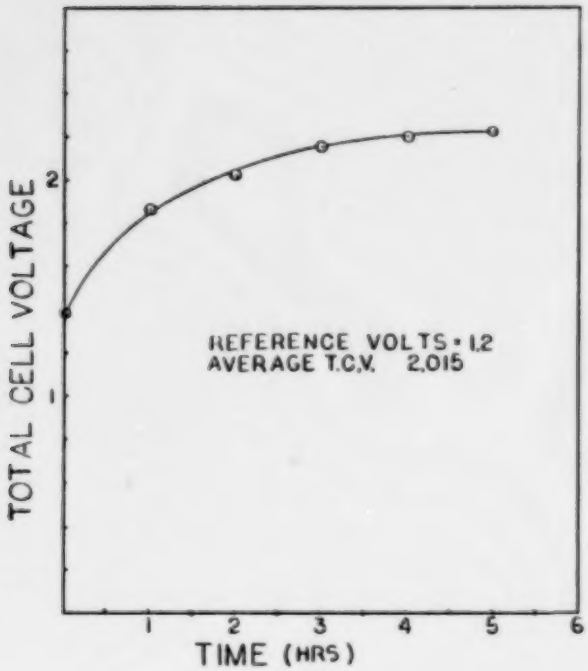
1) 20 liters of sludge at an initial pH of 7.2 required 143.3 ml of 10N $H_2SO_4$ to drop pH to 4.0.

2) Reference electrode shield prevents bubble interference.

3) Working electrodes did not show much visible deposition of any kind. A slight rust colored deposit was seen as well as numerous streaks or scratches up and down the electrode surface with a few going side to side.

4) The contents of the reactor was sampled just before the end of the trial and then again after all the sludge from the electrode carriage, reactor walls etc. were "washed" into the reactor. This will tell if the sludge which accumulates around the electrodes has a high concentration of metals or not. If there is a high concentration of metals the final sample will have a higher metals content than the 5 hour sample.

5) The foam in the reactor was effectively controlled by the mechanical foam-breaker peddle.



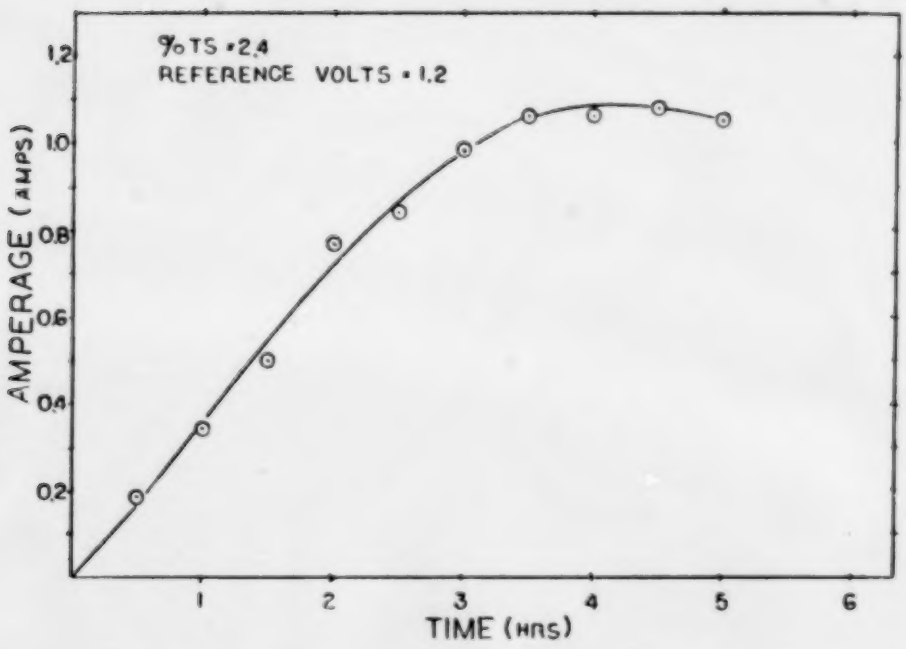




Figure D-1 Sludge Demetalization Test 1

SLUDGE DEMETALIZATION TEST 2 11-12-80

DATA

| Hours Operation | 0 | 1 | 2.5 | 3.5 | 4 | 5 | 6 | 23 |
|---|---|---|---|---|---|---|---|---|
| Time | 10:15 | 11:15 | 12:45 | 1:45 | 2:15 | 3:15 | 4:15 | 9:15 |
| Air Flow (SCFH) | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Sludge Flow (l/min) | 16.32 | 16.32 | 16.44 | 16.32 | 16.56 | 16.44 | 16.32 | 16.68 |
| Temperature (°C) | 45.5 | 51.0 | 53 | 53 | 53.5 | 52.5 | 52 | 52 |
| pH | 4.2 | 4.1 | 4.0 | 3.9 | 3.85 | 3.8 | 3.7 | 3.6 |
| Total Cell Voltage | 1.95 | 2.76 | 2.76 | 2.76 | 2.77 | 2.78 | 2.80 | 2.82 |
| Reference Voltage | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Cell Amperage | (See Chart) | | | | | | | |
| Sample Volume (ml) | 250 | 250 | 250 | 250 | 250 | 250 | 250 | 250 |
| Reactor Volume (l) | 18.65 | 18.4 | 18.15 | 17.90 | 17.65 | 17.4 | 17.15 | 17.8 |
| Acid Volume (ml 10N $H_2SO_4$) | 61 | 10 | 0 | 0 | 0 | 0 | 0 | 0 |

METALS ANALYSIS

| | | MASS (μg) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Cu | Zn | Pb | Ni | Cd | Cr |
| Electrode A | 1st Wash | 158,000 | 300,000 | 13,300 | 14,500 | 4,600 | 48,400 |
| | 2nd Wash | 3,300 | 430 | 190 | 61 | 21 | 38 |
| Electrode B | 1st Wash | 94,400 | 353,000 | 12,100 | 19,400 | 5,000 | 40,000 |
| | 2nd Wash | 750 | 165 | 26 | 15 | 8.5 | 23 |
| Electrode C | 1st Wash | 94,400 | 362,000 | 12,400 | 15,700 | 7,300 | 43,000 |
| | 2nd Wash | 1,300 | 80 | 27 | 22 | 9.0 | 18 |
| Electrode D | 1st Wash | 181,000 | 22,600 | 27,500 | 16,000 | 14,400 | 44,000 |
| | 2nd Wash | 3,500 | 860 | 900 | 140 | 113 | 140 |
| Graphite Electrode | | 40 | 80 | 290 | 16 | 640 | 38 |
| Total(μg) | | 536,690 | 1,039,215 | 66,733 | 65,854 | 32,091.5 | 175,657 |

| Sample | % TS | CONCENTRATION (μg/g solids) Cu | Zn | Pb | Ni | Cd | Cr |
|---|---|---|---|---|---|---|---|
| 0 | 2.060 | 1990 | 5780 | 1800 | 360 | 39 | 920 |
| 1 | 2.079 | 1880 | 4330 | 2100 | 350 | 40 | 1350 |
| 2.5 | 2.056 | 1900 | 3600 | 2330 | 420 | 41 | 1800 |
| 3.5 | 2.053 | 1660 | 2800 | 2040 | 400 | 58 | 1700 |
| 5 | 2.085 | 1770 | 4270 | 2160 | 480 | 33 | 2160 |
| 6 | 2.058 | 1750 | 2500 | 2100 | 400 | 33 | 2480 |
| 23 | 1.828 | 1640 | 2460 | 2100 | 400 | 20 | 4000 |
| Final | 1.858 | 2260 | 1130 | 2150 | 470 | 27 | 3900 |

OBSERVATIONS

1) 18.9 liters of sludge at an initial pH of 6.9 required 61 mls of 10N $H_2SO_4$ to drop pH to 4.0.

2) Reactor sealed with tape to prevent any unnecessary water vapor loss.

3) A 280ml sample of the feed sludge (pH = 6.9) was centrifuged at 3000 rpms for 10 minutes to separate out a supernatant (142 mls) and a thickened solids (38 mls) portion. Each of these (along with the original sludge) was then analyzed for metal content:

| Sample | % TS | CONCENTRATION (mg/l) Cu | Zn | Pb | Ni | Cd | Cr |
|---|---|---|---|---|---|---|---|
| Total Sludge | 2.075 | 51 | 119 | 57 | 9.7 | 0.75 | 26 |
| Supernatant | 0.651 | 49 | 83 | 17 | 8.3 | 0.65 | 10.4 |
| | | MASS (μg) | | | | | |
| Thickened Sludge | 10.19 | 47,700 | 18,900 | 6050 | 1980 | 150 | 5280 |

4) Using a 200 x magnification A/O Dissecting Scope the following observations were made:

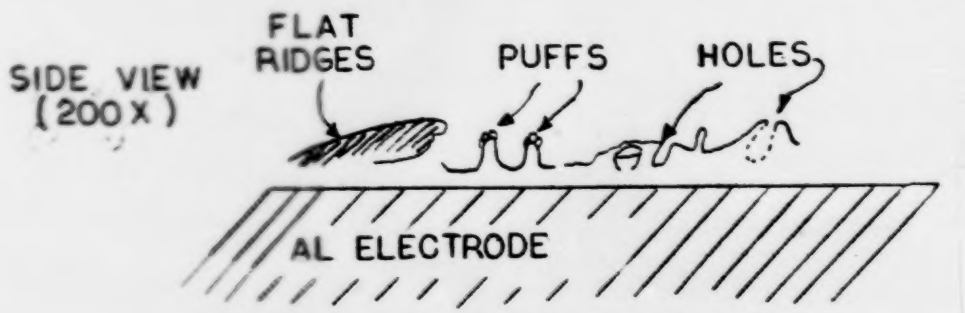



Figure D-2 Al Working Electrode after 23 hrs.

a) Ridges observed to cover approximately 20% of electrode surface, all were rust colored.

b) Puffs observed resembled heads of broccoli and were dark brown in color.

c) Holes were observed interspaced between puffs and seemed to be larger underneath surface.

As the sludge layer was scraped away the underlying particles appeared to be formed of several layers. It seemed that three layers could be identified as in the sketch below:

Figure D-3 Side View of Electrode

layer a) Closest to aluminum surface, this deposit seems very dark brown in color, almost black. This layer does not adhere to the aluminum underneath and can be scraped away easily.

layer b) This layer consists largely of rust colored granules which at various points over the surface "outcrop" to form the ridges in figure 2A.

layer c) Consists of dark brown sludge material in nodules covering 80% of the electrode surface.

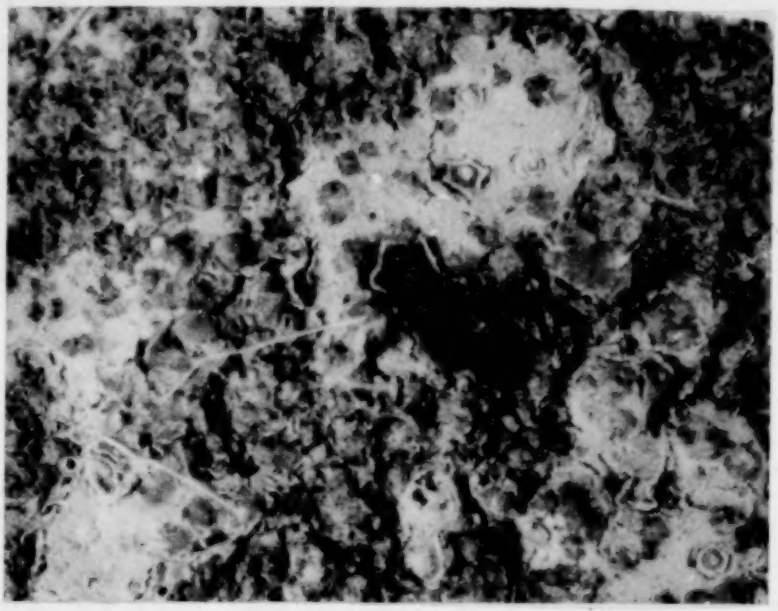
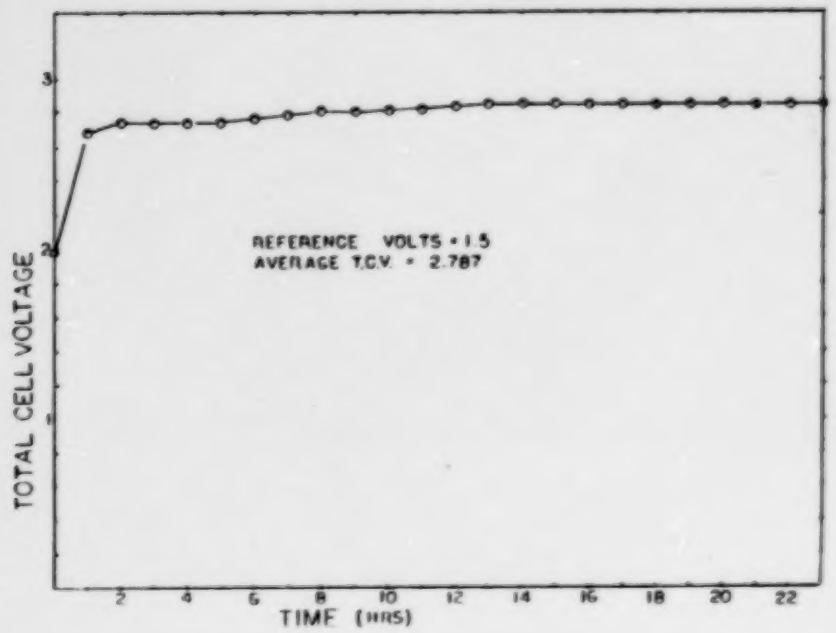


Figure D-4 - Aluminum Electrode Surface (20x)

5) Figure D-4 presents a photograph of the surface of an Aluminum electrode magnified 20X. Although the surface was dry at the time some of the characteristics of figures D-2 and D-3 can be identified. The area identified as a ridge in this photo was made up of orange-rust colored material described previously as layer b. Puffs were more pronounced when electrode surface was wet although the holes can still be seen.



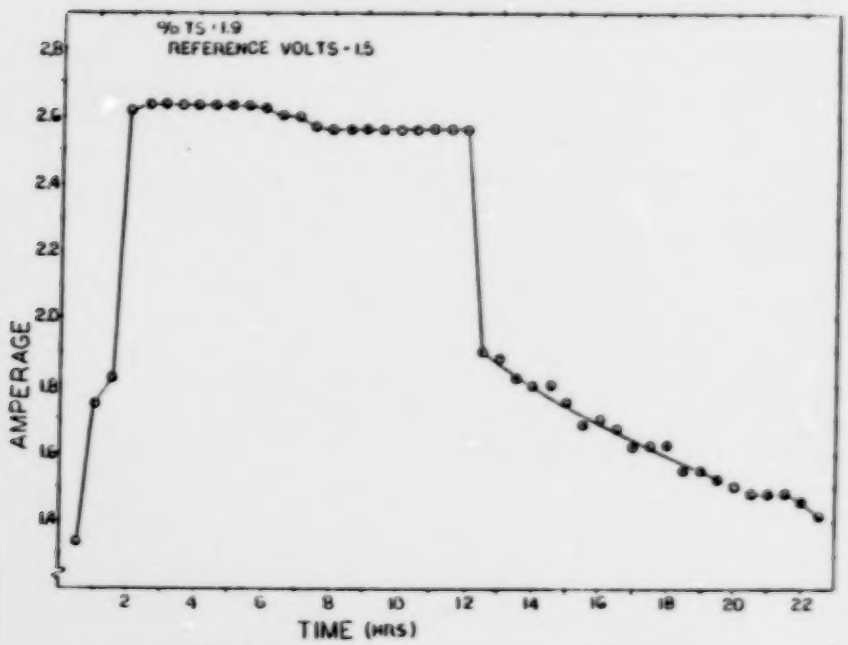




Figure D-5 Sludge Demetalization Test 2

## SLUDGE DEMETALIZATION TEST 3 11-19-80

### DATA

| Hours Operation Time | 0 10:19 | 1 11:19 | 2 12:19 | 3 1:19 | 4 2:19 | 5 3:19 |
|---|---|---|---|---|---|---|
| Air Flow (SCFH) | 5 | 5 | 5 | 5 | 5 | 5 |
| Sludge Flow (l/min) | 16.56 | 16.80 | 16.68 | 16.56 | 16.68 | 16.68 |
| Temperature (°C) | 47.5 | 50.5 | 54 | 54.5 | 54 | 54 |
| pH | 3.90 | 4.45 | 4.0 | 4.0 | 4.0 | 3.95 |
| Total Cell Voltage | 1.85 | 0.80 | 0.67 | 0.66 | 0.65 | 0.65 |
| Reference Voltage | - | 1.50 | 1.50 | 1.50 | 1.51 | 1.50 |
| Cell Amperage | (See Chart) | | | | | |
| Sample Volume (ml) | 250 | 250 | - | 250 | 250 | 250 |
| Reactor Volume (l) | 20.55 | 20.30 | 20.30 | 20.05 | 19.80 | 19.55 |
| Acid Volume (ml 10N $H_2SO_4$) | 50.5 | 10 | 0 | 0 | 0 | 0 |

### METALS ANALYSIS

MASS (µg)

| | Pb | Cd | Ni | Cu | Cr | Zn |
|---|---|---|---|---|---|---|
| Aluminum Electrode | 190 | 24 | 50 | 3960 | 160 | 5160 |
| Graphite Electrode | 1430 | 1300 | 1430 | 24000 | 830 | 68000 |

CONCENTRATION (mg/l)

| Sample | %TS | Pb | Cd | Ni | Cu | Cr | Zn |
|---|---|---|---|---|---|---|---|
| 0 | 1.48 | 31 | 0.63 | 5.9 | 35 | 14 | 57 |
| 5 | 1.53 | 33 | 0.31 | 8.0 | 22 | 23 | 54 |

### OBSERVATIONS

1) 18.8 liters of sludge at an initial pH of 7.5 required 50.5 ml of 10N $H_2SO_4$ to drop pH to 3.90.

2) System is in reverse polarity (i.e. the graphite is acting as the cathode while the aluminum is the anode. The amperage rose dramatically during the first few seconds of the test and then started a steady decline (see chart).

3) One aluminum and one graphite electrode was sent for analysis.

4) The aluminum electrode (anode this experiment) was covered with a network of "puffs" described in Test 2 consisting of white-grey crusty material.

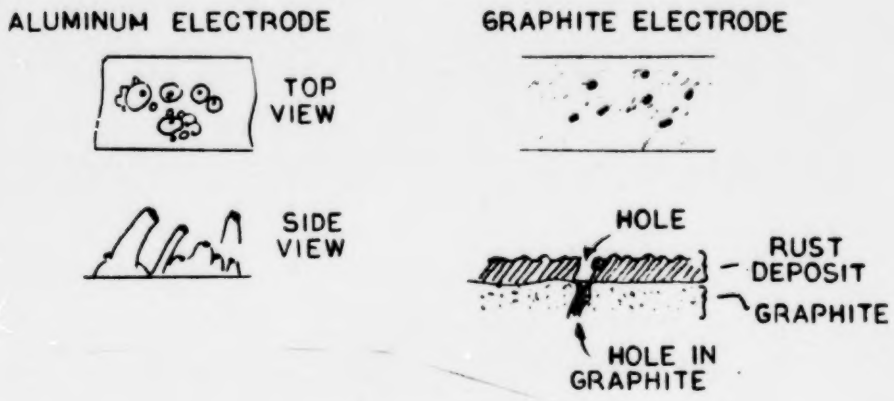
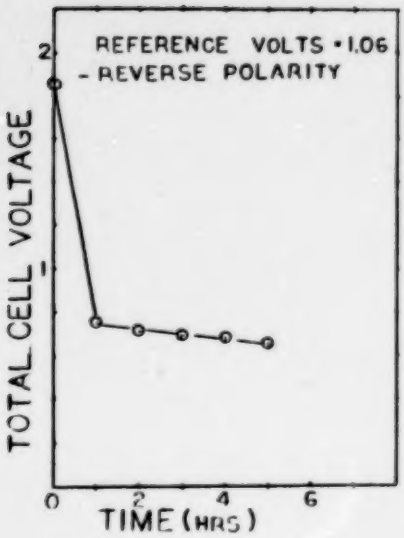



Figure D-6 Electrode Surface Description

The graphite electrode (cathode this experiment) was covered completely with a rust colored pasty substance much like the Aluminum Cathode deposits of Test 2. The covering has holes in it much like the holes in swiss cheese except very small. The holes described here go down all the way to the graphite itself.



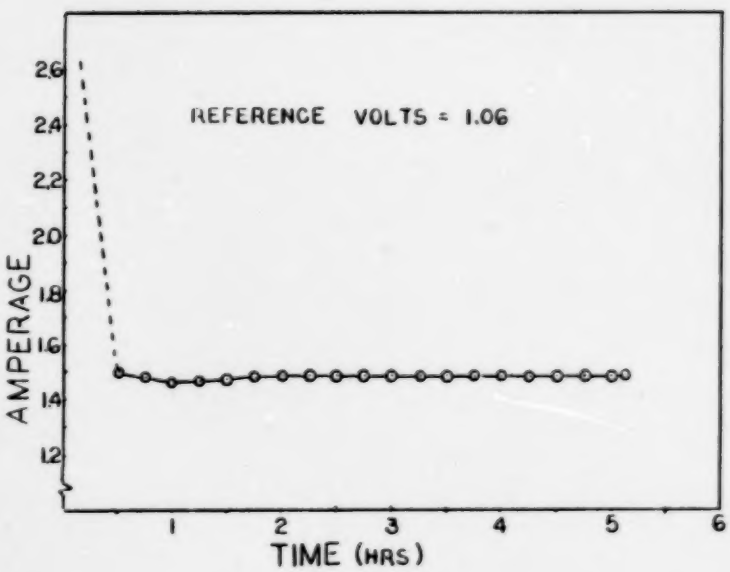




Figure D-7 Sludge Demetalization Test 3

## SLUDGE DEMETALIZATION TEST 4 11-21-80

### DATA

| Hours Operation Time | 0 9:30 | 1 10:30 | 2 11:30 | 3 12:30 | 4 1:30 | 5 2:30 | 6 3:30 |
|---|---|---|---|---|---|---|---|
| Air Flow (SCFH) | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Sludge Flow (l/min) | 16.86 | 16.92 | 16.92 | 16.92 | 16.80 | 16.92 | 17.04 |
| Temperature (°C) | 42 | 44 | 48 | 50 | 49 | 48 | 48 |
| pH | 3.8 | 4.8 | 4.8 | - | 4.0 | 4.0 | 4.0 |
| Total Cell Voltage | 1.25 | 1.61 | 1.77 | 1.88 | 1.98 | 1.99 | 2.0 |
| Reference Voltage | 0.96 | 0.96 | 0.96 | 0.96 | 0.96 | 0.96 | 0.96 |
| Cell Amperage | 0 | 0.155 | 0.155 | 0.65 | 0.63 | 0.565 | 0.54 |
| Sample Volume (ml) | 250 | 250 | 250 | - | 250 | - | 250 |
| Reactor Volume (l) | 19.25 | 19.00 | 18.75 | - | 18.50 | - | 18.25 |
| Acid Volume (ml 10N $H_2SO_4$) | 52 | - | 15 | - | - | - | - |

### METALS ANALYSIS

MASS (μg)

| | Pb | Cd | Ni | Cu | Cr | Zn |
|---|---|---|---|---|---|---|
| Aluminum Electrode | 12000 | 11000 | 66000 | 220000 | 5600 | 62000 |
| Graphite Electrode | 3000 | 2300 | 36 | 22600 | 80 | 4800 |

CONCENTRATION (mg/l)

| Sample | %TS | Pb | Cd | Ni | Cu | Cr | Zn |
|---|---|---|---|---|---|---|---|
| 0 | 1.63 | 35 | 0.67 | 6.8 | 36 | 16 | 58 |
| 1 | 1.60 | 35 | 0.83 | 7.1 | 36 | 16 | 62 |
| 2 | 1.62 | 36 | 0.85 | 7.9 | 32 | 19 | 61 |
| 4 | 1.66 | 34 | 0.84 | 8.2 | 24 | 24 | 56 |
| 6 | 1.68 | 34 | 0.86 | 9.2 | 24 | 20 | 65 |

### OBSERVATIONS

1) When acid was added at 11:30 the current jumped from 0.155 to 0.900 amps. The current then slowly dropped thereafter to 0.65 amps (see chart).

2) All the graphite electrodes seemed very clean with no deposits. The aluminum cathodes were coated with very fine particulate matter that seemed to form two layers of slightly different color (see sketch).

3) After drying overnight one of the aluminum electrodes was photographed. Much of the material clinging to the electrodes flaked off after drying into a large tray. Therefore all the electrodes will be combined into a single wash solution for analysis.

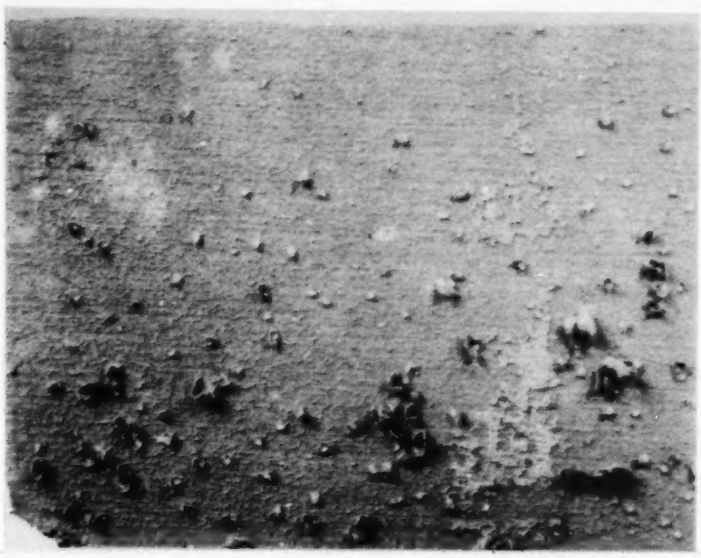


Figure D-8 Aluminum electrode, Magnification 15X

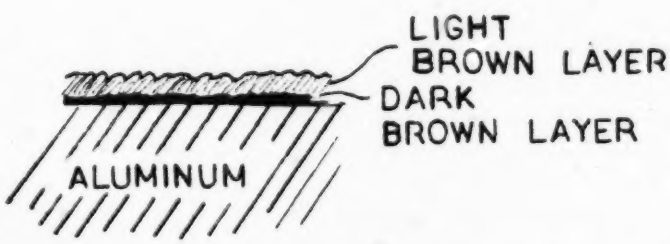
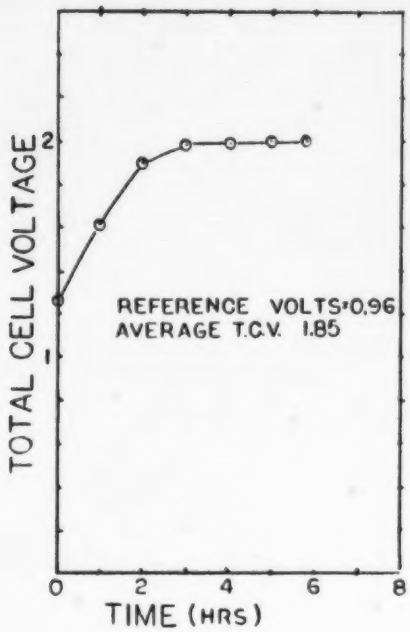



Figure D-9 Sketch of Electrode Deposit



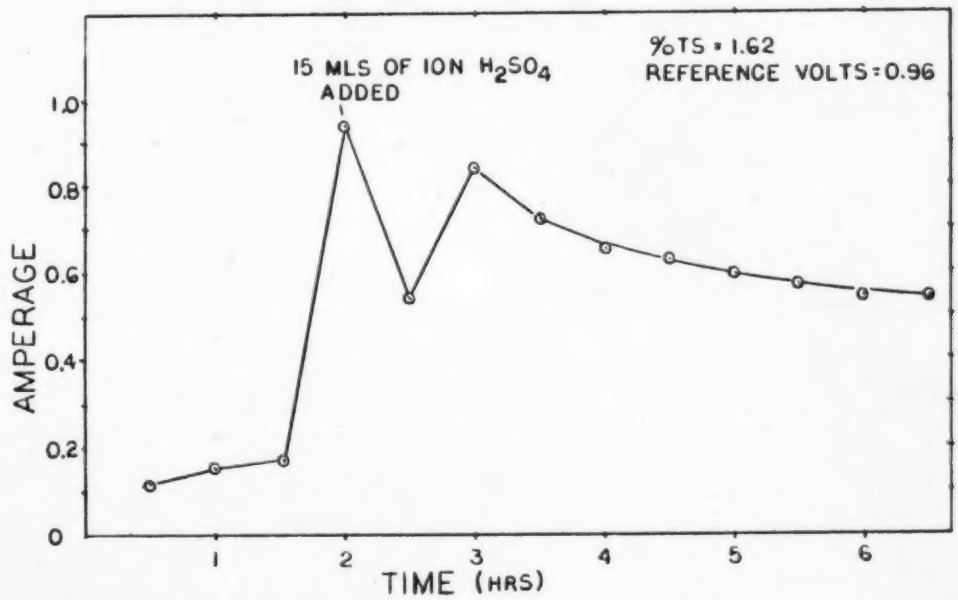




Figure D-10 Sludge Demetalization Test 4

## SLUDGE DEMETALIZATION TEST 5 12-17-80

### DATA

| Hours Operation Time | 0 9:25 | 1 10:25 | 2 11:25 | 3.5 1:00 | 5 2:25 | 7 4:25 | 23 8:25 |
|---|---|---|---|---|---|---|---|
| Air Flow (SCFH) | 4.0 | 4.0 | 4.8 | 4.0 | 4.0 | 4.0 | 4.0 |
| Sludge Flow (l/min) | 27.84 | 28.32 | - | 26.88 | 27.12 | 26.88 | 27.50 |
| Temperature (°C) | 54 | - | - | - | 49 | 48.5 | 48 |
| pH | 4 | 4.4 | 52 | 4.4 | 4.0 | 3.9 | 3.7 |
| Total Cell Voltage | 2.14 | 2.44 | 2.50 | 2.62 | 2.65 | 2.64 | 2.73 |
| Reference Voltage | 1.504 | 1.504 | 1.504 | 1.504 | 1.504 | 1.504 | 1.504 |
| Cell Amperage | - | 0.55 | 0.65 | 0.70 | 0.70 | - | 0.50 |
| Sample Volume (ml) | 300 | - | - | - | - | 300 | 300 |
| Reactor Volume (l) | 17.7 | 17.7 | 17.7 | 17.7 | 17.7 | 17.4 | 17.1 |
| Acid Volume (ml 10N $H_2SO_4$) | 65.5 | - | - | 12 | 10 | - | - |

### METALS ANALYSIS

MASS (µg)

| | Pb | Ni | Cd | Cr | Zn | Cu |
|---|---|---|---|---|---|---|
| Electrode Total | 4680 | 3950 | 16600 | 3580 | 206000 | 99000 |

CONCENTRATION (mg/g Solids)

| Sample | %TS | Pb | Ni | Cd | Cr | Zn | Cu |
|---|---|---|---|---|---|---|---|
| 0 | 1.96 | 30.0 | 8.5 | 0.50 | 18.2 | 64.6 | 36.0 |
| 7 | 1.88 | 29.8 | 8.1 | 2.30 | 18.0 | 61.0 | 33.0 |
| 23 | 1.86 | 33.0 | 8.1 | 3.30 | 23.0 | 67.0 | 38.0 |
| Final | 1.67 | 16.4 | 3.8 | 1.52 | 11.0 | 29.0 | 15.8 |

### OBSERVATIONS

1) 18 liters of sludge at an initial pH of 7.85 required 65.5 ml of 10N $H_2SO_4$ to drop pH to 4.0.

2) All metal fittings in sludge recirculation loop have been replaced by their plastic counterparts. A new pump (March Model AC-SC-MD, 1/8 HP, magnetic drive) with a barium ferrite magnet coated with GE insulating enamel was used.

3) 25 mls of high temperature (U.C.C. L-720) silicon based anti-foam agent was added to the reactor. No appreciable foam problem was then encountered.

4) There was some sludge buildup on the top of the distribution manifold which was washed into the final sample.

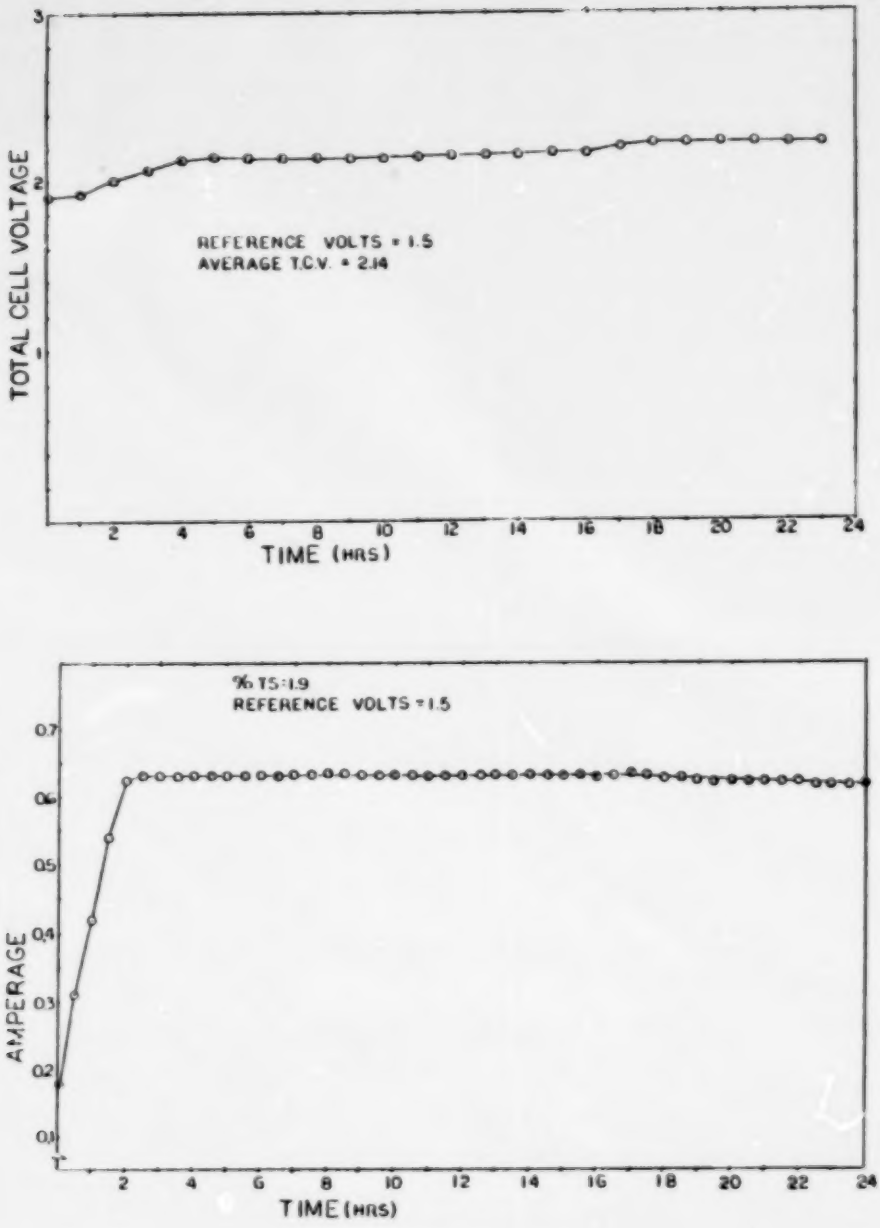



Figure D-11 Sludge Demetalization Test 5

## SLUDGE DEMETALIZATION TEST 6 1-6-81

### Data

| Hours Operation | 0 | 7 | 24 |
|---|---|---|---|
| Time | 9:40 | 4:40 | 9:40 |
| Air Flow (SCFH) | 4 | 4 | 4 |
| Sludge Flow (l/min) | 50 | 50 | 50 |
| Temperature (°C) | 44 | 50 | 50 |
| pH | 3.60 | 3.75 | 3.40 |
| Total Cell Voltage | 2.76 | 2.86 | 2.84 |
| Reference Voltage | 1.504 | 1.504 | 1.504 |
| Cell Amperage | 1.95 | 1.68 | 1.23 |
| Sample Volume (ml) | | | |
| Reactor Volume (l) | 18.27 | 18.02 | 17.77 |
| Acid Volume (ml 10N $H_2SO_4$) | 55 | 0 | 0 |

### METALS ANALYSIS

MASS (µg)

| | Zn | Cu | Cd | Ni | Pb | Cr |
|---|---|---|---|---|---|---|
| Total Electrodes | 300,000 | 660,000 | 29,000 | 30,000 | 54,000 | 15,000 |

CONCENTRATION (mg/l)

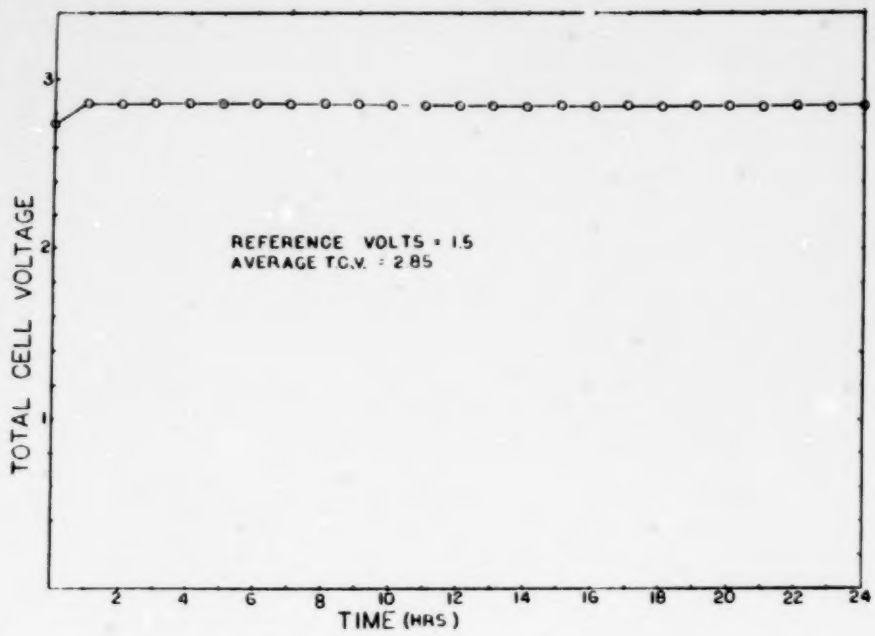
| Sample | %TS | Zn | Cu | Cd | Ni | Pb | Cr |
|---|---|---|---|---|---|---|---|
| 0 | 1.14 | 33 | 20 | 0.46 | 3.0 | 15 | 14 |
| 7 | 1.10 | 25 | 7.4 | 0.32 | 2.2 | 14 | 14 |
| 24 | 1.09 | 23 | 3.6 | 0.12 | 1.6 | 11 | 14 |
| Final | 1.09 | 22 | 2.9 | 0.35 | 1.6 | 11 | 13 |

### OBSERVATIONS

1) 18.46 liters of sludge at an initial pH of 8.15 required 55 ml of 10N $H_2SO_4$ to drop pH to 3.5.

2) The reactor contained about 12 stainless steel screws and one brass elbow which was not in the mainstream of the sludge flow pattern. This could account for some of the remaining discrepancies in the metals balance.

3) The graphite electrical connections were modified so as to eliminate the use of alligator clips which were found to be seriously corroded following Test 5. The clips (figure 21 in text) had "holes" in them as well as extensive surface attack. The new method of attachment involves drilling holes into the graphite anode, inserting, the connecting wire and sealing the connection with silicone adhesive.



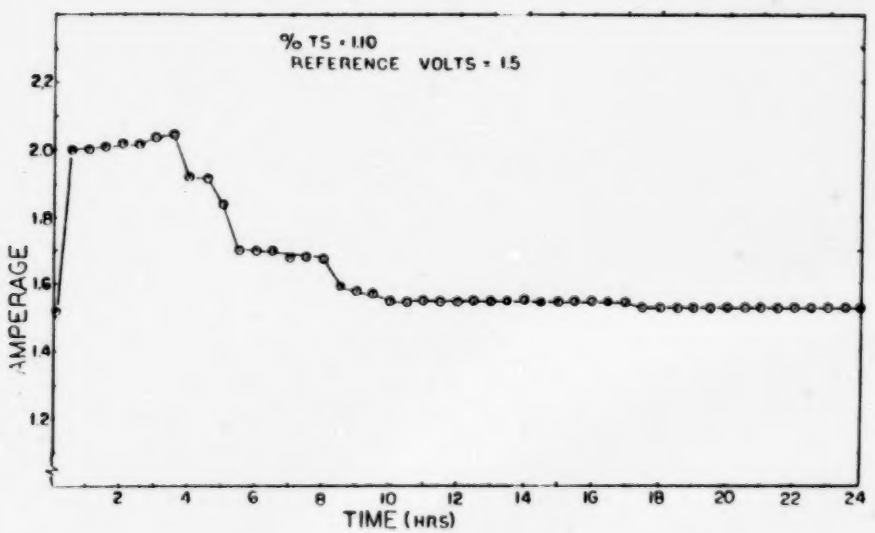




Figure D-12 Sludge Demetalization Test 6

## SLUDGE DEMETALIZATION TEST 7 1-12-81

### Data

| Hours Operation | 0 | 18 | 24 |
|---|---|---|---|
| Time | 2:30 | 8:30 | 2:30 |
| Air Flow (SCFH) | 4 | 4 | 4 |
| Sludge Flow (l/min) | 25.56 | 27.72 | 24.65 |
| Temperature (°C) | 47 | 47 | 47.5 |
| pH | 3.75 | 3.75 | 3.80 |
| Total Cell Voltage | 3.43 | 3.39 | 3.38 |
| Reference Voltage | 2.00 | 2.00 | 2.00 |
| Cell Amperage | 3.30 | 3.25 | 3.15 |
| Sample Volume (ml) | 0 | 250 | 250 |
| Reactor Volume (l) | 17.74 | 17.49 | 17.24 |
| Acid Volume (ml 10N $H_2SO_4$) | 63.5 | 0 | 0 |

### METALS ANALYSIS

MASS (µg)

| | Cu | Cd | Ni | Zn | Cr | Pb |
|---|---|---|---|---|---|---|
| Total Electrodes | 180,000 | 1,700 | 45,000 | 160,000 | 3,500 | 5,300 |

CONCENTRATION (mg/l)

| Sample | %TS | Cu | Cd | Ni | Zn | Cr | Pb |
|---|---|---|---|---|---|---|---|
| 0 | 1.83 | 25 | 0.24 | 6.2 | 41 | 15 | 22 |
| 18 | 1.67 | 16 | 0.33 | 3.3 | 31 | 12 | 20 |
| 23 | 1.67 | 16 | 0.33 | 1.7 | 29 | 13 | 21 |
| Final | 1.76 | 16 | 0.36 | 0.9 | 30 | 14 | 21 |

### OBSERVATIONS

1) 19.29 liters of sludge at an initial pH of 6.75 required 63.5 ml of 10N $H_2SO_4$ to drop pH to 3.75.

2) Note that pressure gauge in recirculation system is metal and may contaminate sludge. It will be removed prior to Test 8.

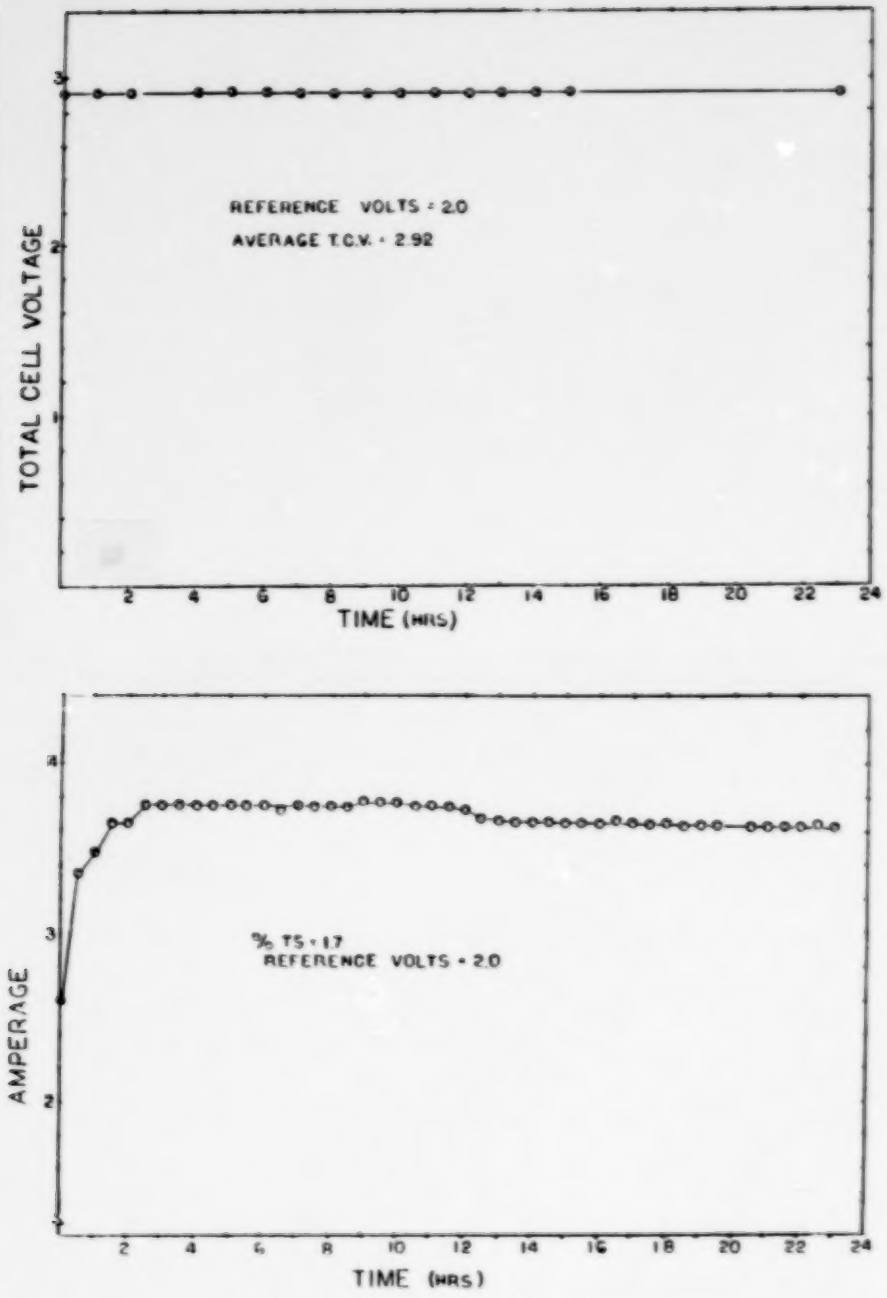



Figure D-13 Sludge Demetalization Test 7

## SLUDGE DEMETALIZATION TEST 8 1-20-81

### Data

| Hours Operation Time | 0 | 6 | 23 |
|---|---|---|---|
| Air Flow (SCFH) | 4 | 4 | 4 |
| Sludge Flow (l/min) | 27.54 | 27.60 | 25.95 |
| Temperature (°C) | 41 | 48.5 | 47.5 |
| pH | 4.0 | 4.55 | - |
| Total Cell Voltage | 2.19 | 2.55 | 2.72 |
| Reference Voltage | 1.30 | 1.30 | 1.30 |
| Cell Amperage | 0.29 | 0.72 | 0.95 |
| Sample Volume (ml) | 250 | 250 | 500 |
| Reactor Volume (l) | 18.03 | 17.78 | 16.47 |
| Acid Volume (ml 10N $H_2SO_4$) | 85 | 15 | 0 |

### METALS ANALYSIS

MASS (µg)

| | Cd | Cu | Ni | Pb | Cr | Zn |
|---|---|---|---|---|---|---|
| Total Electrodes | 4,500 | 700,000 | 49,000 | 53,000 | 3,300 | 100,000 |

CONCENTRATION (mg/ml)

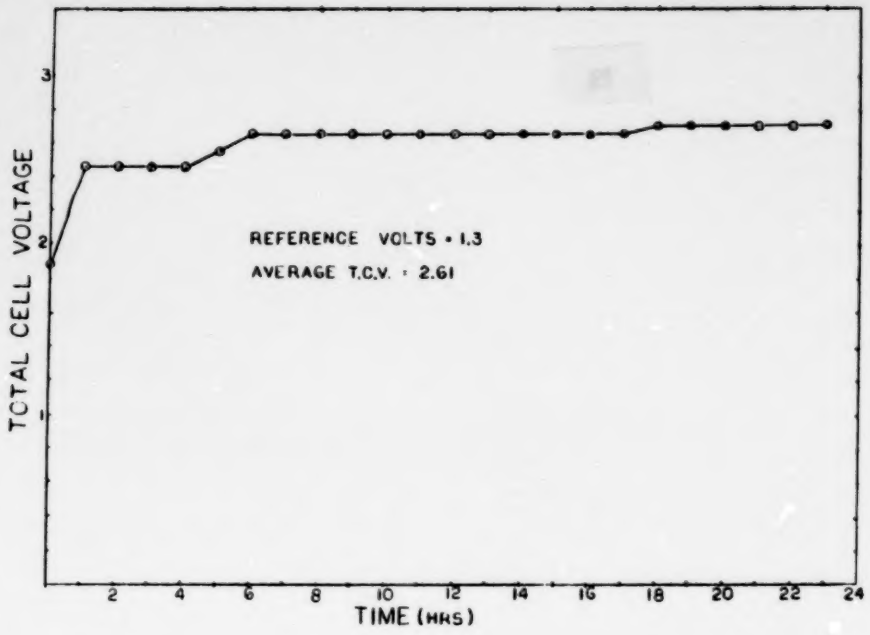
| Sample | %TS | Cd | Cu | Ni | Pb | Cr | Zn |
|---|---|---|---|---|---|---|---|
| 0 | 2.10 | 0.40 | 38 | 6.5 | 46 | 14 | 100 |
| 6 | 1.98 | 0.22 | 26 | 5.7 | 39 | 13 | 76 |
| 14 | 1.94 | 0.14 | 11 | 4.3 | 41 | 12 | 56 |
| 24 | 1.94 | 0.15 | 11 | 3.9 | 44 | 12 | 56 |
| Final | 2.04 | 0.21 | 12 | 4.2 | 43 | 14 | 65 |
| Test | - | 91 | 0 | 0 | 0 | 0 | 100 |

### OBSERVATIONS

1) 20.2 liters of sludge at an initial pH of 7.6 required 85 ml of 10N $H_2SO_4$ to drop pH to 4.0.

2) Upon addition of 15 ml of acid at 6 hours, the amperage rose dramatically from 0.72 amps to 1.10 amps (see chart).

3) Test solution of Cd and Zn salts analyzed.



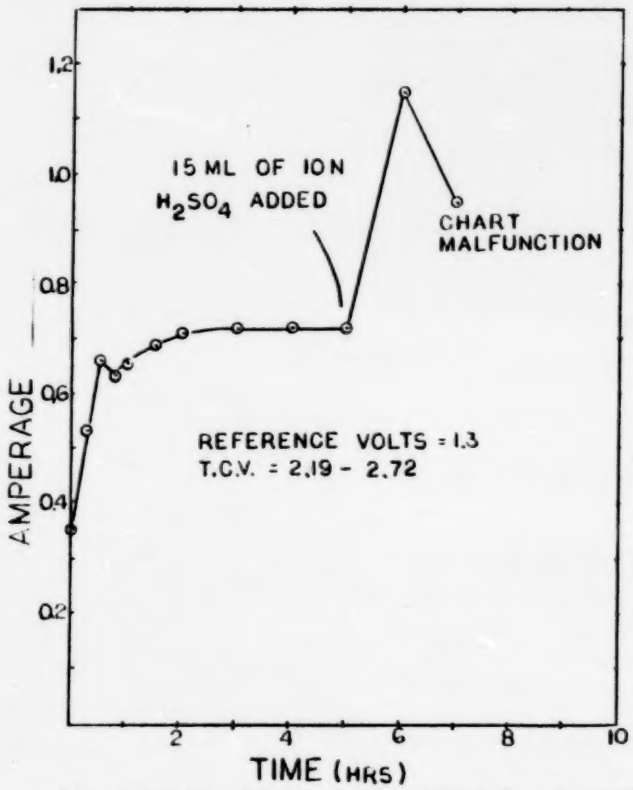




Figure D-14 Sludge Demetalization Test 8

## SLUDGE DEMETALIZATION TEST 9 1-26-81

### Data

| Hours Operation | 0 | 1 | 24 |
|---|---|---|---|
| Time | 3:00 | 4:00 | 3:00 |
| $N_2$ Flow (SCFH) | 4 | 4 | 4 |
| Fluid Flow (l/min) | 48.0 | 49.5 | 49.3 |
| Temperature (°C) | 28.5 | 34.5 | 44.5 |
| pH | 3.84 | - | - |
| Total Cell Voltage | 2.00 | 2.50 | 2.43 |
| Reference Voltage | 1.30 | 1.30 | 1.30 |
| Cell Amperage | 0.270 | 0.355 | 0.389 |
| Sample Volume (ml) | 250 | 250 | 500 |
| Reactor Volume (l) | 20.0 | 19.75 | 17.25 |

### OBSERVATIONS

1) Reactor was washed with hot water and Alconox and all hoses cleaned. Reactor was then washed with tap water and rinsed with distilled water. The reactor was then filled with 10N $H_2SO_4$ which was allowed to recirculate for approximately 1 hour. Finally the reactor was rinsed twice with distilled water.

2) Gas agitation was switched to nitrogen.

3) The test solution was made up of known amounts of $ZnSO_4$ and $CdSO_4$ dissolved in distilled water.

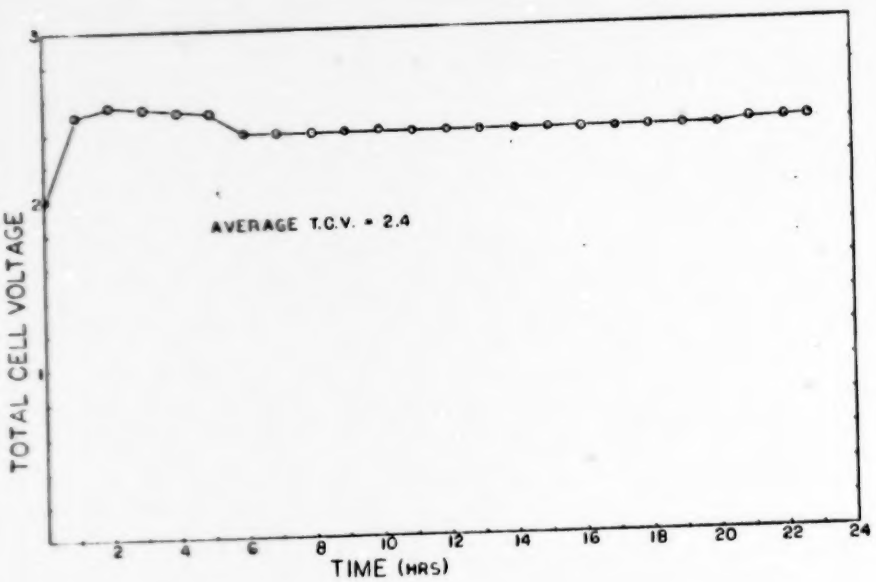



Figure D-15 Sludge Demetalization Test 9

## SLUDGE DEMETALIZATION TEST 10 1-29-81

### Data

| Hours Operation | 0 | 1 | 6 | 24 |
|---|---|---|---|---|
| Time | 10:13 | 11:13 | 4:13 | 10:13 |
| $N_2$ Flow (SCFH) | 4 | 4 | 4 | 4 |
| Sludge Flow (l/min) | 27.12 | 27.32 | 27.10 | 25.60 |
| Temperature (°C) | 21.5 | 32.0 | 46.0 | 46.0 |
| pH | 3.85 | - | 3.80 | - |
| Total Cell Voltage | (See Chart) | | | |
| Cell Amperage | (See Chart) | | | |
| Sample Volume (ml) | 250 | - | - | 250 |
| Reactor Volume (l) | 20.75 | 20.75 | 20.50 | 20.25 |

### METALS ANALYSIS

MASS (μg)

| | Cd | Zn | Cu | Ni | Ci | Pb |
|---|---|---|---|---|---|---|
| Total Electrodes | 1,040,000 | 94,000 | 4,800 | 25 | 85 | 1,500 |

CONCENTRATION (mg/ml)

| Sample | Cd | Zn | Cu | Ni | Ci | Pb |
|---|---|---|---|---|---|---|
| Initial | 96 | 106 | 0.1 | 0.1 | 0.1 | 0.1 |
| 0 | 97 | 104 | 0.1 | 0.1 | 0.1 | 0.1 |
| 6 | 78 | 107 | 0.6 | 0.1 | 0.1 | 0.1 |
| 24 | 22 | 98 | 1.3 | 0.1 | 0.1 | 0.1 |

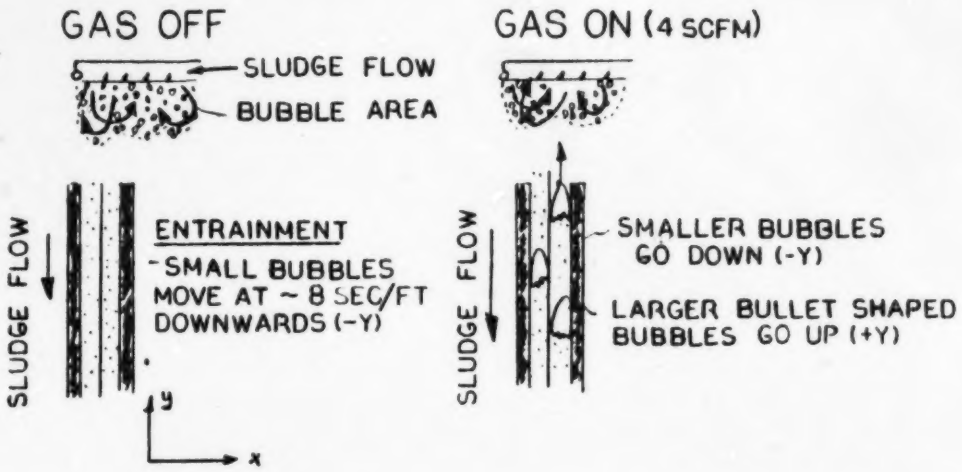
### OBSERVATIONS

1) In this test $ZnSO_4$ and $CdSO_4$ were added to distilled water to make up a solution containing approximately 100 ppm of each metal ion. This was done to provide a "clean" solution with which to determine a metals balance for the reactor.

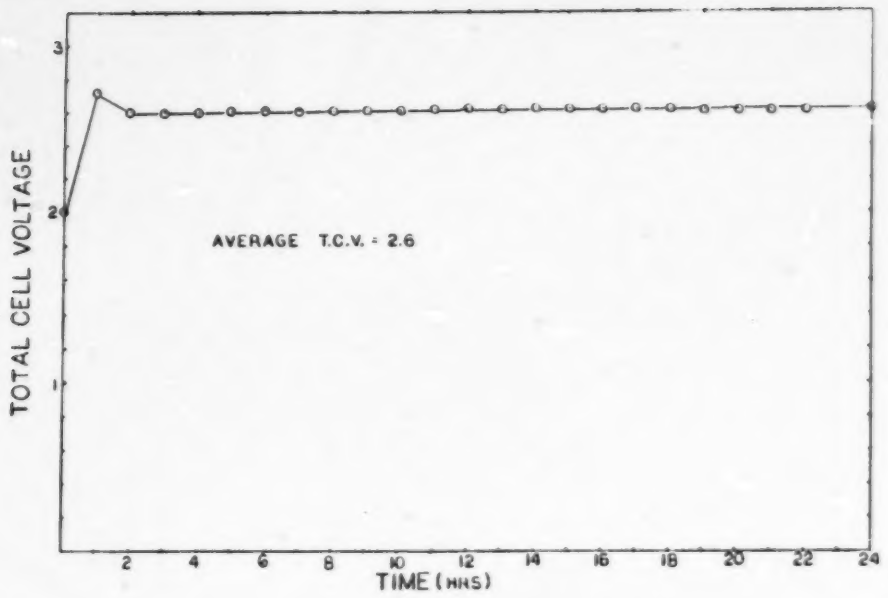
2) The reactor was cleaned according to the procedure described in Test 9.

3) Some problems were encountered with the integrating recorder for total cell amperage. The unit was replaced after approximately 20 minutes of operation.

4) The nitrogen gas used for agitation purposes was turned off for a short while and the following observations made:




5) A photograph at 15x magnification of the Aluminum electrode surface after 24 hours of plating in synthetic solution.



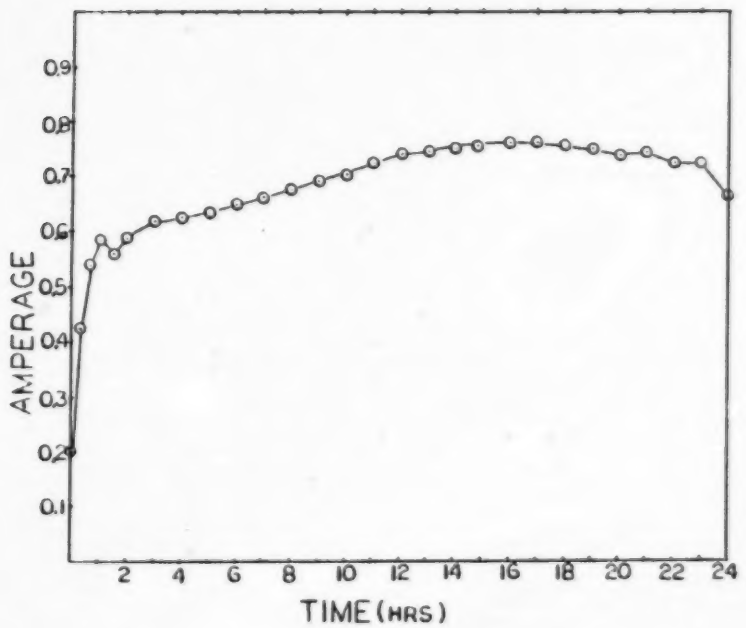




Figure D-16 Sludge Demetalization Test 10

## SLUDGE DEMETALIZATION TEST 11 2-2-81

### Data

| | | |
|---|---|---|
| Hours Operation | 0 | 24 |
| Time | 2:30 | 2:30 |
| $N_2$ Flow (SCFH) | 4 | 4 |
| Temperature (°C) | 21.5 | 45.5 |
| pH | 2.95 | 2.90 |
| Reactor Volume (l) | 18.86 | 18.31 |

### METALS ANALYSIS

MASS (µg)

| | Cd | Zn | Cu | Ni | Cr | Pb |
|---|---|---|---|---|---|---|
| Total Electrodes | 560,000 | 680 | 440,000 | 25 | 120 | 2100 |

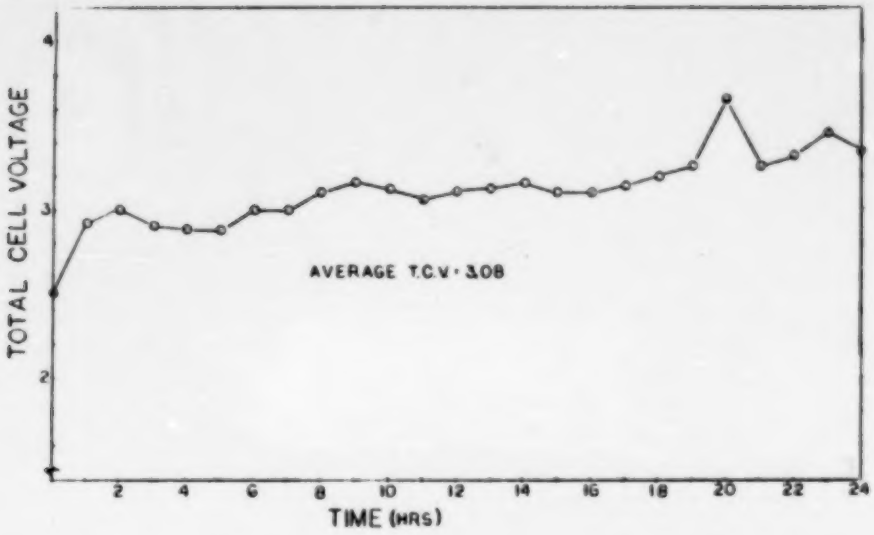
CONCENTRATION (mg/l)

| Sample | Cd | Zn | Cu | Ni | Ci | Pb |
|---|---|---|---|---|---|---|
| Initial | 94 | 98 | 88 | 100 | 0.1 | 0.1 |
| 0 | 92 | 98 | 88 | 96 | 0.1 | 0.1 |
| 24 | 28 | 98 | 14 | 96 | 0.1 | 0.1 |

### OBSERVATIONS

1) Synthetic solution was made up in a 25l batch of distilled water with the following dissolved salts.

| Formula | Mol Wt. | Element Wt. | Wt. Ratio | Wt. Needed (g) |
|---|---|---|---|---|
| $CdSO_4$ | 208.5 | 112.4 | 1.855 | 4.64 |
| $CuSO_4$ | 159.6 | 63.55 | 2.511 | 6.28 |
| $NiSO_4\ 6H_2O$ | 267.5 | 58.7 | 4.478 | 11.19 |
| $ZnSO_4\ 7H_2O$ | 287.5 | 65.37 | 4.399 | 11.00 |



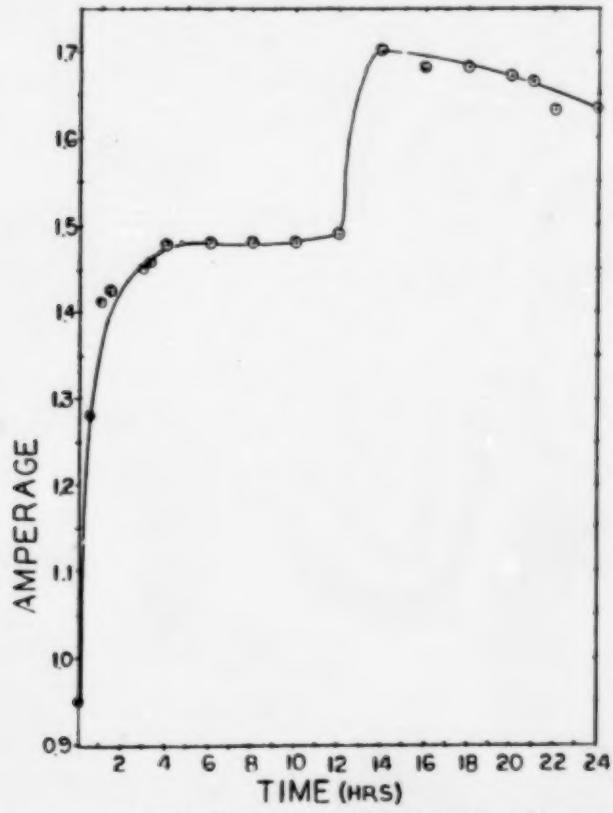




Figure D-17 Sludge Demetalization Test 11

## DEMETALIZATION TEST 12 2-9-81

### Data

| | | | |
|---|---|---|---|
| Hours Operation | 0 | 16 | 23 |
| Time | 4:00 | 8:00 | 3:00 |
| $N_2$ Flow (SCFH) | 4 | 4 | 4 |
| Fluid Flow (l/min) | 45.6 | 53.7 | 52.5 |
| Temperature (°C) | 20.0 | 49.0 | 49.5 |
| pH | 2.75 | 2.55 | 2.50 |
| Total Cell Voltage | 3.37 | 3.07 | - |
| Total Cell Amperage | (See Chart) | | |
| Reactor Volume (l) | 18.50 | 18.25 | 17.52 |

### METALS ANALYSIS

MASS (µg)

| | Cu | Cd | Ni | Zn | Pb | Cr |
|---|---|---|---|---|---|---|
| Total Electrodes | 810,000 | 1,000,000 | 11,500 | 725 | 450 | 100 |

CONCENTRATION (mg/l)

| Sample | Cu | Cd | Ni | Zn | Pb | Cr |
|---|---|---|---|---|---|---|
| Initial | 84 | 87 | 80 | 95 | 0.1 | 0.1 |
| 0 | 80 | 85 | 74 | 89 | 0.1 | 0.1 |
| 16 | 11 | 28 | 72 | 88 | 0.1 | 0.1 |
| 24 | 8 | 28 | 76 | 96 | 0.1 | 0.1 |

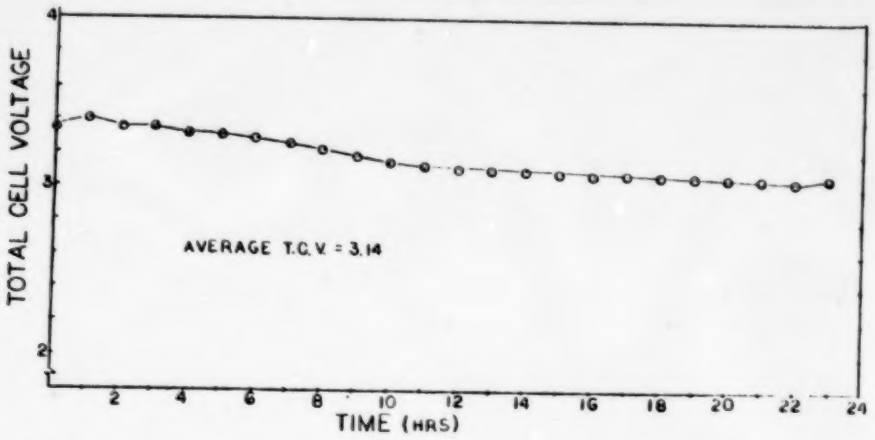
### OBSERVATIONS

1) Same metals solution as Test 11 was prepared.

2) In this test brand new graphite electrodes just cut from a large block on the machine shop bond-saw were used. Graphite was acid washed and then drilled and tapped to accommodate an 1/8" diameter, threaded graphite rod. The anode was then assembled as per figure (22) in the text of this report and was electrically connected approximately 8" above the fluid surface with the connection being sealed with silicone rubber adhesive. These precautions were taken to insure no contamination from the alligator clips.

3) No gas seemed to be evolving from either the anode or the cathode during this test.

4) Around one graphite block a noticeable difference in the appearance of an accompanying aluminum electrode pair was observed. The two cathode sides facing the graphite block in question had deposits which were red in color ($FeO_2$?) as compared to the other aluminum surfaces which were black in color. The graphite block was checked for continuity at the end of the test and found to be properly connected.



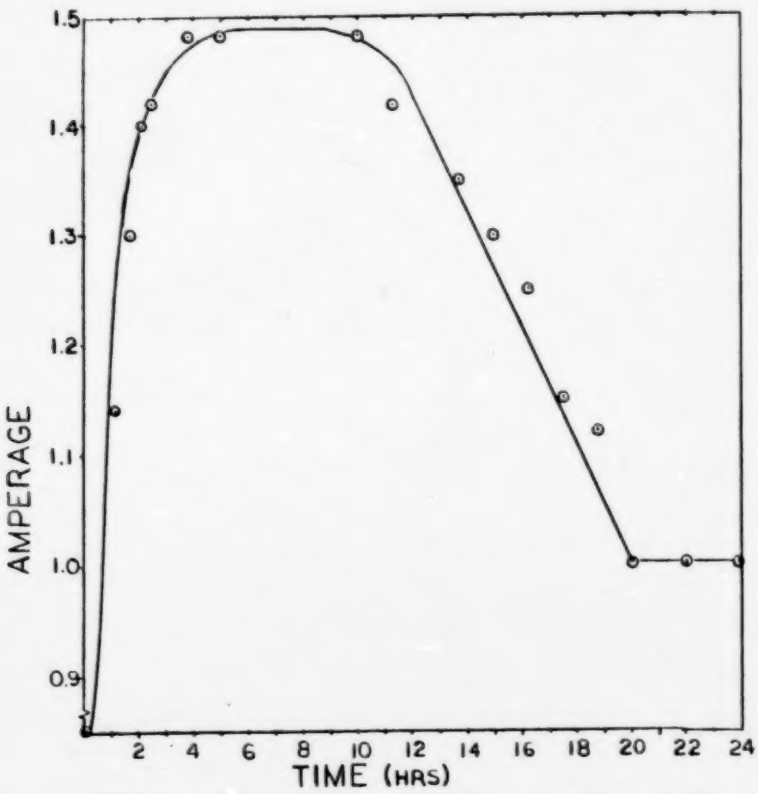




Figure D-18 Sludge Demetalization Test 12

## DEMETALIZATION TEST 14 2-24-81

### Data

| Hours Operation | 0 | 17 | 22 |
|---|---|---|---|
| Time | 4:00 | 9:00 | 2:00 |
| $N_2$ Flow (SCFH) | 4 | 4 | 4 |
| Fluid Flow (l/min) | 44.85 | 45.3 | 45.0 |
| Temperature (°C) | 28 | 49.5 | 50.0 |
| pH | 2.35 | 2.30 | 2.32 |
| Reference Voltage | 1.40 | 1.40 | 1.40 |
| Reactor Volume (l) | 17.53 | - | 16.98 |

### METALS ANALYSIS

| | MASS (μg) | |
|---|---|---|
| | Cd | Zn |
| Filter Paper #1 | 3,200 | 730 |
| Filter Paper #2 | 3,100 | 110 |
| Total Electrodes | 1,100,000 | 7,300 |

### OBSERVATIONS

1) Metal solution was prepared similar to that of Test 11.

2) When reactor was shut down at the end of 22 hours the following steps were taken to capture any plated metals which may have spalled off the electrodes:

a) Clean glassware with acid and distilled water.

b) Weigh and record filter paper weights.

c) Keeping power on, slowly drain reactor through filter paper into a 2 liter graduate and from there into a large holding bottle.

d) Pour approximately 20 l of distilled water into reactor and recirculate to mix contents. Drain this volume through a second piece of filter paper.

e) Dry filter papers and send to laboratory along with electrodes.

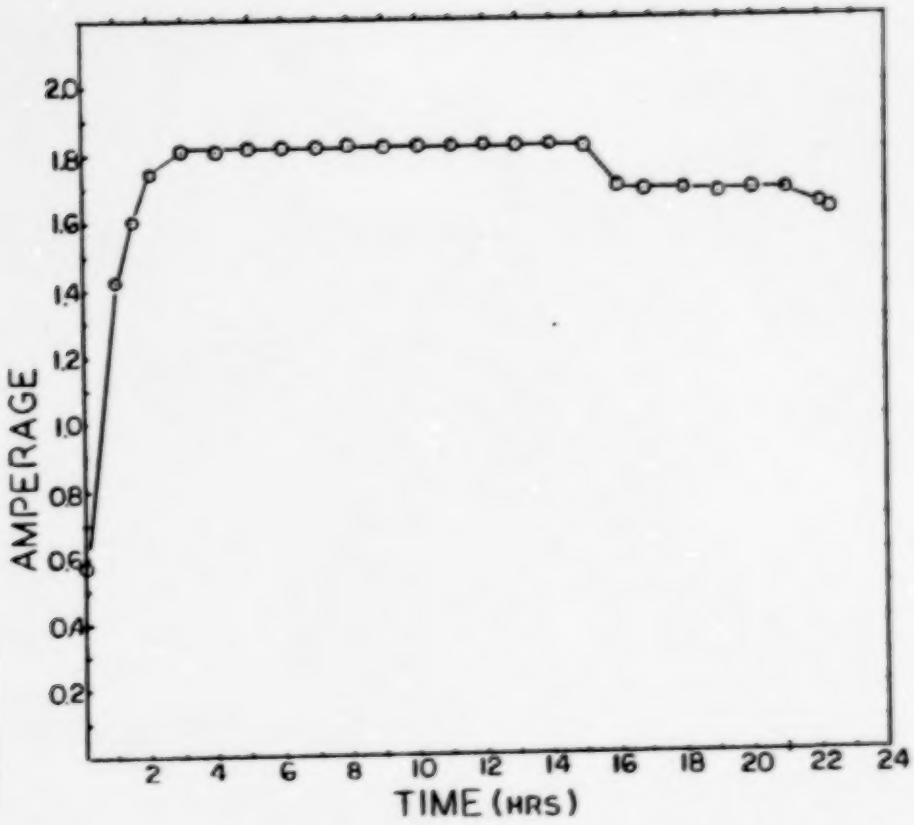



Figure D-19 Sludge Demetalization Test 14

## DEMETALIZATION TEST 15 3-9-81

### Data

| Hours Operation | 0 | 2 | 23 |
|---|---|---|---|
| Time | 2:00 | 4:00 | 1:00 |
| $N_2$ Flow (SCFH) | 4 | 4 | 4 |
| Fluid Flow (l/min) | 33.15 | - | 33.15 |
| Temperature (°C) | 46 | 47 | 48 |
| pH | 3.0 | 3.1 | 2.9 |
| Total Cell Voltage | 1.46 | 1.46 | 1.46 |
| Reference Voltage | 1.40 | 1.40 | 1.40 |
| Cell Amperage | 1.0 | 1.1 | 1.0 |
| Sample Volume (ml) | 200 | 200 | 200 |
| Reactor Volume (l) | 19.56 | 19.36 | 19.16 |

### METALS ANALYSIS

| | MASS (mg) | |
|---|---|---|
| | Cd | Zn |
| Wash Residue | 1,680 | 79 |
| Test Residue | 69,000 | 150 |
| Total Electrodes | 1,110,000 | 200,000 |

| Sample | CONCENTRATION (mg/l) | |
|---|---|---|
| | Cd | Zn |
| 0 | 93.5 | 70.4 |
| 2 | 26.2 | 67.9 |
| 23 | 0.42 | 59.6 |
| End | 0.49 | 56.2 |

### OBSERVATIONS

1) Solution make up of approximately 100 ppm each of Cd $SO_4$ and Zn $SO_4$ in distilled water.

2) Shut down procedure outlined in Test 14 was again followed in order to capture stray solids.

3) Upon removal of electrode assembly, deposits (orange-yellow in color) were found only on one side of each cathode.

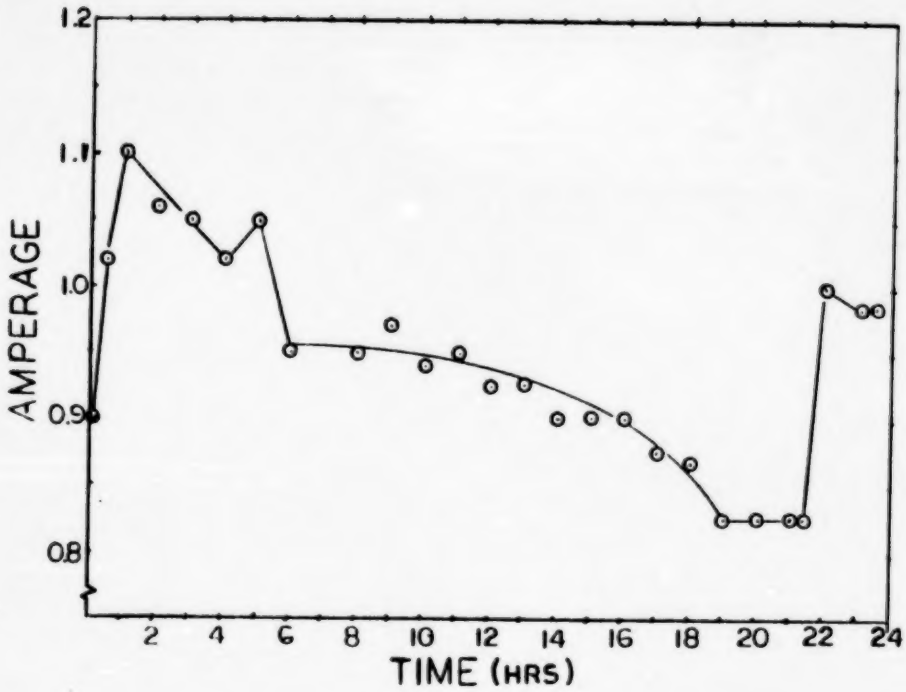



Figure D-20 Sludge Demetalization Test 15

## DEMETALIZATION TEST 16 4-9-81

### Data

| | | | |
|---|---|---|---|
| Hours Operation | 0 | 15:5 | 19 |
| Time | 3:30 | 7:00 | 10:30 |
| $N_2$ Flow (SCFH) | 4 | 3 | 3.5 |
| Fluid Flow (l/min) | 5.4 | - | 5.4 |
| Temperature (°C) | 30 | - | 43 |
| pH | 4 | - | 3.3 |
| Total Cell Voltage | 2.8 | 3.1 | 3.16 |
| Reference Voltage | 1.401 | 1.402 | 1.402 |
| Cell Amperage | 0.05 | 0.09 | 0.09 |
| Sample Volume (ml) | 200 | - | 200 |
| Reactor Volume (l) | 21.38 | - | 21.18 |

### METALS ANALYSIS

| | MASS (µg) | |
|---|---|---|
| | Cd | Zn |
| Filter Paper #1 | 8,200 | 460 |
| Filter Paper #2 | 7,600 | 1,500 |
| Total Electrodes | 533,000 | 1,200 |

| Sample | CONCENTRATION (mg/l) | |
|---|---|---|
| 0 | 80 | 88 |
| 19 | 50 | 84 |
| End | 53 | 92 |

### OBSERVATIONS

1) Solution make up of approximately 100 ppm each of Cd $SO_4$ and Zn $SO_4$ in distilled water.

2) Shut down procedure outlined in Test 14 followed.

3) Low fluid recirculation rate reduces the liquid head above the distribution manifold. Result is an increase in gas entrainment at this point.

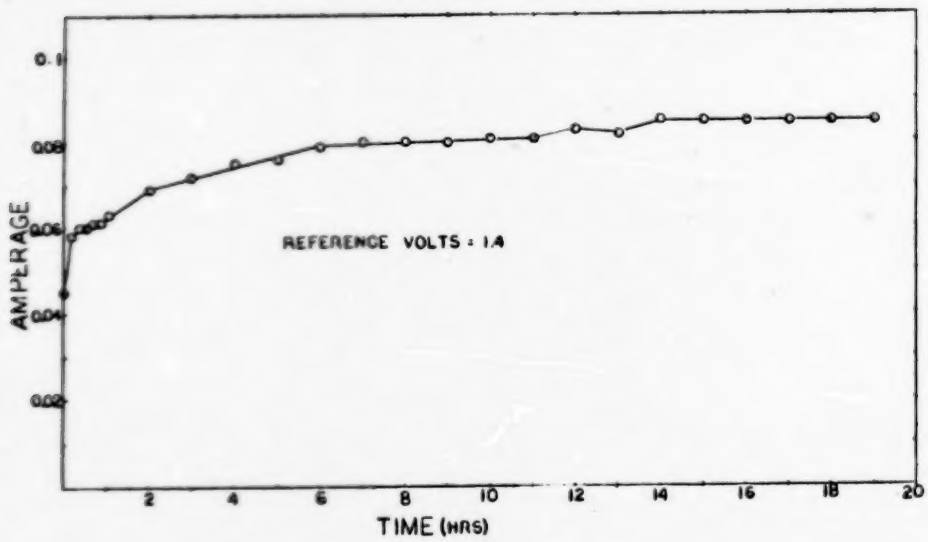



Figure D-21 Sludge Demetalization Test 16

DEMETALIZATION TEST 17 4-9-81

Data

| Hours Operation | 0 | 21 |
|---|---|---|
| $N_2$ Flow (SCFH) | 4 | 4 |
| Fluid Flow (l/min) | 5.4 | 5.4 |
| Temperature (°C) | 30 | 46 |
| pH | 6.0 | 6.0 |
| Total Cell Voltage | 2.20 | 2.80 |
| Reference Voltage | 1.401 | 1.401 |
| Cell Amperage | 0.60 | 2.10 |
| Sample Volume (ml) | 300 | 300 |
| Reactor Volume (l) | 19.50 | 19.05 |

METALS ANALYSIS

| | Mass (µg) Cd | Zn | |
|---|---|---|---|
| Total Electrodes | 4,000 | 31,600 | |
| Filter Paper | 2,600 | 12,700 | |
| Sample | Concentration (mg/l) | | |
| Feed Sludge | 1.0 | 35.0 | 1.25 |
| Sludge Supernatant | 0 | 1.12 | - |
| Sludge Solids | 82.8 | 2700 | - |
| 0 | 0.86 | 20.5 | - |
| 21 | 0.56 | 18.4 | - |
| End | 0.80 | 19.7 | - |

OBSERVATIONS

1) Secondary sludge was thermophilically digested and then centrifuged. The decanted supernatant was used as the demetalization test solution.

2) Extreme difficulty was encountered in filtering the test and wash solutions due to sludge particles clogging filter pores. Solutions were instead gravity settled and the resulting liquid drawn off and filtered.

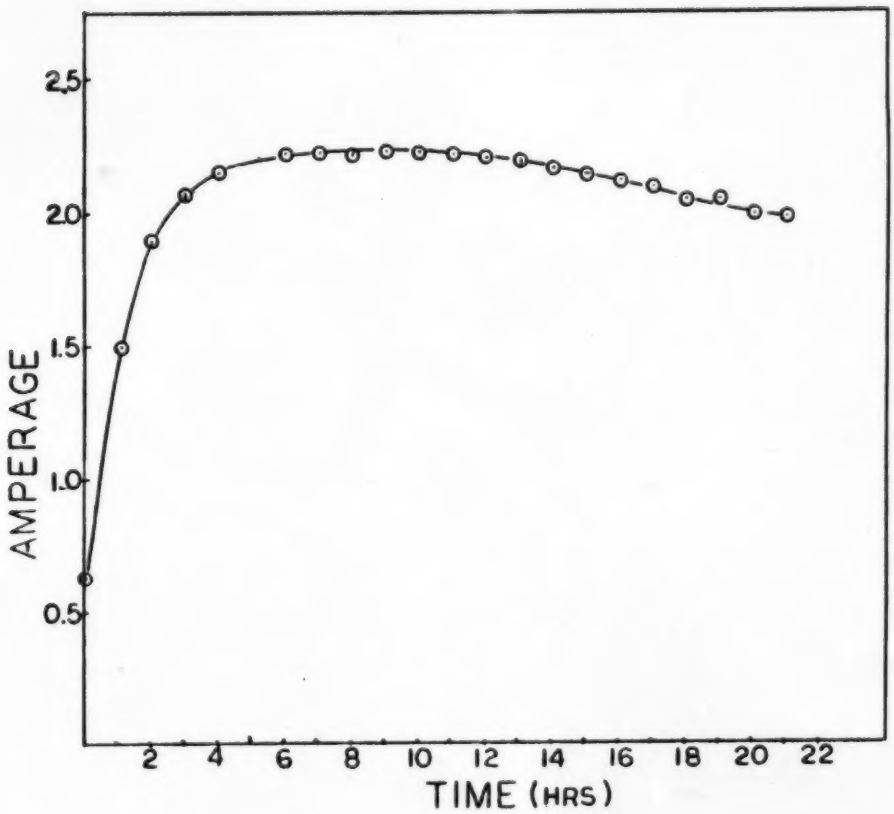



Figure D-22 Sludge Demetalization Test 17